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Three-Level Maser Materials: A Survey of Potential Materials, I

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ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

In 1956 Townes et al.[1] proposed and successfully produced
an oscillator which utilized the induced emission from an
excited quantum energy state. It was named the maser. A
brief sketch of its principles is as follows.

Two quantum energy states exist. The difference in their
energies is ΔE. In the presence of an electromagnetic field, a
system in the lower energy state will absorb energy from the field
at a rate A which is sharply peaked when the incident field is of the
frequency $f = \dfrac{\Delta E}{h}$, where h is Planck's constant. This rate is propor-
tional to the square of either the electric or magnetic field strength.
Similarly, a system in the upper energy state emits energy to
the field at the same rate A in the same frequency and direc-
tion as the incident field. If an ensemble is composed of a
mixture of systems in the lower and upper energy states, then
the ensemble's absorption is $A(n_1 - n_2)$, where n_1 is the number of
particles in the lower state and n_2 is the number of particles
in the upper energy state.

If we wish to make an amplifier, we must obtain from
such a device a field which is larger than the field which we feed
into the device. In a maser, this means that there should be
a net emission of energy by the system into the field. This
requires that $A(n_1 - n_2)$ must be negative or that $n_2 > n_1$. If the
device were lossless, we would have an amplifier whenever this
requirement is fulfilled. In practice, $A(n_1 - n_2)$ must be sufficiently
negative to overcome inevitable losses. For an oscillator,
$A(n_1 - n_2)$ must be negative enough to overcome not only its own
losses but the losses in the load as well.

At thermal equilibrium, the lower energy state is always
more heavily populated than the upper state. The ratio is given

by Boltzmann's distribution

$$\frac{n_2}{n_1} = e^{-\Delta E/kT}$$

Therefore, some process is required to upset this thermal equilibrium before a maser can be made to operate. This process is called inversion (because it inverts the population of the states at thermal equilibrium) or pumping.

In the first maser due to Gordon, Zeiger, and Townes, a beam of ammonia molecules passed through a multipole electric field with a gradient which deflects high energy molecules differently from the low energy molecules. Thus, a separation of high and low energy molecules is achieved. This creates a beam of molecules in which $\frac{n_2}{n_1} >> 1$. This beam satisfies the condition for a maser. This beam is passed on into a cavity which is tuned to the transition frequency $f = \frac{\Delta E}{h}$, where h is Planck's constant. If the Q is high enough to give A (the transition probability) its proper value, maser oscillation or amplification takes place.

The maser aroused great interest because of two advantages.

(1) As an oscillator it has very great stability.

(2) As an amplifier it has a much lower noise figure than that of vacuum tubes or transistors.

These advantages were demonstrated by both theory and experiments.

The success of the first maser naturally stimulated vigorous efforts to improve its characteristics. The ammonia maser had a low power-handling capacity. One way to overcome this characteristic is to use a solid as the maser material. The higher density of active atoms would allow both higher power capacity and compactness. Zeeman levels of paramagnetic ions in solids provide convenient energy levels for masers in the microwave frequency range.[4,5]

In such a maser, a dielectric solid, containing a small amount (typically .05%) of paramagnetic centers, is subject to a strong d. c. magnetic field. The magnetic moment due to electron spin interacts with the magnetic field to give an energy $g\beta \overline{H} \cdot \overline{S} \cdot$, where g and β are constants, $\overline{H}$ is the d. c. magnetic field, and $\overline{S}$ is the electron spin. Discrete quantum energy levels result from the discrete quantum orientations of $\overline{S}$ with respect to $\overline{H}$. Such levels can be inverted by several methods developed in the study of nuclear magnetism. Examples are adiabatic fast passage (AFP), 180° pulse inversion or d. c. field reversal.

These masers can generate a moderate amount of peak power but have the serious drawback that they can only be operated as pulsed devices. This is because the inversion process and maser process can never be simultaneous . First, an inversion process is applied. When this process is over, the maser process takes over. The maser process can last only as long as the state of inversion exists. As the maser process proceeds, inversion is reduced until the maser process is no longer possible. The system must then be allowed to relax to thermal equilibrium before the inversion process is applied again. Because of this limitation, the two-level solid state maser is considered now only as a measure to reach the millimeter wave region by pulsed d. c. magnetic fields. [2, 3]

In 1957 Bloembergen[4] proposed a new type of maser which could be operated continuously. Briefly, the principle was as follows.

An atom has three quantum energy states with energies E_1, E_2, and E_3, respectively. The energy differences are ΔE_{21}, ΔE_{32} and ΔE_{31} as in Fig. 1. At thermal equilibrium, the probability of occupation of the three levels is given by Boltzmann's distribution. Each higher level has a smaller population then its lower neighbor.
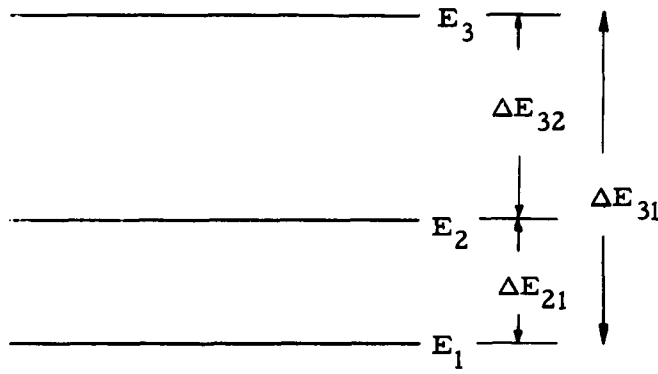
Figure 1

Now, if a strong electromagnetic field of frequency $f = \dfrac{\Delta E_{31}}{h}$ is applied induced transition causes atoms at E_1 to be excited to E_3 and atoms at E_3 to be de-energized to E_1. This is called pumping. The induced transition rates per atom for these two processes are equal for these equally degenerate states. The net rate is then given by $A(n_1 - n_3)$, where A is induced transition rate and n_1 and n_3 are the number of units at energy E_1 and E_3, respectively. If this rate A is very much larger than the mechanisms which promote thermal equilibrium, a steady state is achieved when $A(n_1 - n_3) = 0$. Therefore, with strong inducing fields, $n_1 = n_3$. This condition is called saturation. If, furthermore, A is very much larger than the mechanisms (relaxation) which bring E_1 and E_3 into thermal equilibrium with E_2, and these mechanisms are of equal strength for E_1 and E_3, the population of E_2 will remain approximately at its value before pumping. This value is $n_2 = n_1^o e^{-\Delta E_{21}/kT}$, where n_1^o is the thermal equilibrium value of n_1.

$$\text{After pumping, } n_1 = \frac{n_1^o + n_1^o e^{-\Delta E_{31}/kT}}{2} = \frac{n_1^o}{2}(1 + e^{-\Delta E_{31}/kT}).$$

If $\Delta E_{31}/kT << 1$, $n_2 = n_1^o(1 - \Delta E_{21}/kT)$, $n_1 = n_3 = n_1^o/2\,(2 - \Delta E_{31}/kT)$ $= n_1^o(1 - \Delta E_{31}/2kT)$. Therefore, inversion is achieved between levels E_3 and E_2 if $\Delta E_{31} < 2\Delta E_{21}$. If $\Delta E_{31} > 2\Delta E_{21}$, inversion is achieved

between levels E_2 and E_1. If the relaxations to E_2 from E_1 and E_3 are not equal, the relations are modified to give

$$n_3 - n_2 = \frac{N}{3kT} \frac{-\omega_{23}\Delta E_{32} + \omega_{21}\Delta E_{21}}{\omega_{23} + \omega_{12} + W_{32}}$$

where ω_{ij} is the relaxation rate from level i to level j. Bloembergen suggested $5\%Ni95\%ZnSiF_6 \cdot 6H_2O$ and $1\%Gd99\%La(C_2H_5SO_4)_3 \cdot 9H_2O$ as possible material for his maser.

The three-level maser, as Bloembergen's device is called, was first successfully operated by McWhorter and Myers[6] using the Zeeman levels of Cr^{3+} in $KCr(CN_6)$. Kikuchi et al. [7] constructed a more successful model using the Zeeman levels of Cr^{3+} in Al_2O_3 (ruby). Ruby masers are now in practical operation as radio-astronomical preamplifiers at microwave frequencies.

The success of the ruby maser naturally turned the attention of researchers to other materials which might be suited for three-level masers. Ruby is an excellent material. However, practical operation is limited to below approximately 10 kmc. There exists a need for oscillators and amplifiers at higher frequencies. It is also desirable to operate masers without liquid helium. * The search for new materials is to an extent guided by

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* Maiman (70) in Quantum Electronics Conference has reported that ruby masers have been successfully operated at liquid nitrogen and dry ice temperatures. There are no reports of its practical use. It should be noted that if a maser material is suited for operation at liquid nitrogen temperature, then it can be made to perform even better at liquid helium. Therefore, it is possible that masers will always be operated at liquid helium temperature as long as it is available. The cryogenics involved is expensive and inconvenient from the point of view of technical application.

these two considerations. So far, the search has turned up five promising materials. They are beryl,[8] TiO_2 (rutile),[9,10,11] $MgWO_4$, $ZnWO_4$, and $CaWO_4$ (calcium tungstate or scheelite[12,13]). The first two materials are capable of operation well into the millimeter wave region. The tungstates are suitable for use in the $10 - 40$ kmc range. SnO_2 is also reported to be under investigation.

CHAPTER II

PARAMAGNETIC RESONANCE IN CRYSTALS:
A REVIEW

The susceptibility of solids differs from that of free atoms (gas) in that the atoms are ionized in the solid and that these ions have considerably modified orbital states as the result of the electric field set up by the other ions in the crystal. Most ions have complete shells. Thus, they are diamagnetic. The ions with incomplete shells can be paramagnetic. If they were not subject to the crystalline electric field, the paramagnetism would have contributions from both the orbital and spin magnetic moments of the ion. However, in many cases the crystalline field "quenches" the orbital moment and leaves a paramagnetism which is due to spin alone.

The energy levels used in the three-level maser are the Zeeman levels of the lowest orbital state of a paramagnetic ion in a solid. (Higher energy levels cannot be used because only a very small percentage of the ions are in such states, particularly at low temperatures.) The study of maser materials is, therefore, the study of the lowest energy levels of paramagnetic ions in crystals.

The theory of paramagnetism in solids was pioneered by Van Vleck[15] in the 1930's. Considerable theoretical development also took place in Holland in the 1930's and 1940's. In fact,

a firm basis of the present theory was well established during this early period. It is a very remarkable achievement when one considers the fact that the only source of experimental data were susceptibility measurements. They were not able to observe the energy levels directly by microwave resonance as we do today.

A new approach to the problem was opened by Zaviosky[16] in 1945, when he was able to observe microwave paramagnetic resonance of electrons. Since then, the field has progressed very rapidly. The major part of the work in the field in the last ten years has been in England. Good, organized accounts of the present approach to the theory are given by Bleaney and Stevens[17] and by Low.[18] Experimental results have been collected by Bowers and Owens[20] and by Orton.[21] More recently, Koster[19] has developed a new theory based on group theory. The general theory of atomic spectra is covered completely by Condon and Shortley.[22] The theory of transitions metal spectra, in particular, is covered by J. S. Griffith.[78] These theories are retraced in some detail in this chapter.

II. 1 The Hamiltonian for a Paramagnetic Ion in a Crystal

Any discussion of quantum energy levels must begin with the Hamiltonian. The Hamiltonian for a paramagnetic ion in a crystal is given by

$$H = \sum_i \left(\frac{P_i^2}{2m} - \frac{Z\ell^2}{r_i^2} \right) + \sum_{i > j} \frac{\ell^2}{r_{ij}^2} + V_{cryst.} + \sum_{ij} \lambda_{ij} \vec{\ell}_i S_j$$

$$+ \sum_i \vec{H} \cdot (\vec{\ell}_i + 2S_i) \mu_B$$

(2. 1)

The first term is the kinetic energy of the electrons and the potential energy of the electrons in the field of the nucleus. The second term is the potential energy of the electrons in the fields of each other. The third term is the potential energy of the electrons in the field of the surrounding crystal. The fourth is the spin-orbit coupling energy. The last term is the Zeeman energy.

This Hamiltonian is too complex to be solved exactly for the eigenstates and eigenenergies. In order to use perturbation methods, the relative magnitudes of the various terms in the Hamiltonian must be established. The largest terms are the first and second terms. The relative magnitudes of the remaining terms depend on the ion in question and its environment.

For the rare earths, it is agreed that the order of the interactions in descending magnitude is electron-electron interaction (called Coulomb interaction), spin-orbit coupling, followed by the crystalline field interaction and the Zeeman energy. The crystalline field has a relatively weak effect because the electrons which give rise to paramagnetism in the rare earths are shielded by an outer complete shell.

In the iron group the situation is not clear cut. The electrons which contribute to paramagnetism are the outermost electrons. They feel the full effect of the crystalline field. Consequently, the crystalline field interaction is comparable to the electron-electron Coulomb interaction. In fact, in many cases it exceeds an important part of the Coulomb interaction so that researchers have differed in their approach to the problem. Bleaney and Stevens[17] treat the crystalline field as a perturbation on the Coulomb interaction. This same approach was taken by Van Vleck et al.[15] in the early analysis of alums. This approach is outlined in some detail in this chapter.

Other researchers have approached this problem by considering the crystalline field to be more important than the

non-central field part of the Coulomb interaction. This is some-
times referred to as the crystalline field representation. Examples
are the presentation of paramagnetic resonance by Bowers and
Owens.[20] In ruby, for example, the optical spectrum is discussed
more readily by the crystalline field representation. Practically
all current literature on the optical spectrum of ruby is given in
this manner. Low[23] has also discussed this problem. He finds
that the crystalline field is of such magnitude that it causes a
considerable mixing of eigenstates in the LS coupling scheme where
representation is diagonal in the Coulomb interaction Hamiltonian.

Since we are interested mainly in the paramagnetism
of the iron group, the case of the rare earths is omitted from
further discussion. We will now proceed with the discussion of
the energy levels in the iron group.

Even with perturbation methods, the total Hamiltonian
(2.1) is still too complex to solve exactly. Therefore, a
simplifying approximation is made in the treatment of the
Coulomb interaction.

II. 2 The Configuration

The simplification is to replace the electron-electron
electrostatic energy as an equivalent central-field potential
energy. This is not an inverse square-law type potential. It
decreases much more rapidly with increasing r (the distance
from the nucleus). When this is done, the term can be lumped
with the nucleus-electron energy to give

$$\sum_i \left(\frac{P_i^2}{2m} + V_i(r)l \right) \tag{2.2}$$

for the first three terms. These two terms are the largest
terms in the Hamiltonian. Therefore, this partial Hamil-
tonian can be solved for eigenstates and eigenenergies which,
in turn, can be used as the basis for perturbation calculations
of the states and energies for the complete Hamiltonian.

This partial Hamiltonian does not involve electron-electron interactions. Thus, the equation is separable in the coordinates of each electron. The eigenfunction is the product of single electron eigenfunctions, and the energy is the sum of individual electron energies.

The single-electron eigenfunction in the central-field potential without an inverse square dependence on r differs from the inverse square (hydrogen atom) case in that the energy is a function of l , the orbital angular momentum quantum number. The quantum numbers are still n (radial quantum number), l (orbital angular momentum quantum number), m_l (z-component of orbital angular momentum), and m_s (z-component of spin).

The group of all states having the same quantum numbers n and l is called a shell. A shell is of particular significance because of several reasons. When all states in the shell are occupied, the electrostatic potential due to the electrons in the shell becomes isotropic (spherically symmetric). The total orbital and total spin angular momenta of the electrons in the shell become zero. Therefore, ions with full shells are diamagnetic.

The eigenfunction for atoms or ions with more than one electron can be formed as a combination (product) of single electron eigenfunctions. We are interested in the ground state (lowest energy eigenfunction). This might be formed by taking the lowest energy state for each electron, were it not for Pauli's exclusion principle which prohibits such a combination.

The exclusion principle by Pauli states that no two electrons can occupy identical eigenstates. An alternate statement is that electron eigenfunctions must be anti-symmetric with respect to permutations of the electrons.

The lowest energy state of a many-electron atom is then constructed by filling the single-electron eigenstates of the

atom one by one, starting with the lowest energy
state and moving upward in energy until all the electrons are
assigned to a state. This means that we start with states of
lowest n first. Among states of the same n, the states of lowest
ℓ usually have the lowest energy.[*] Such combination states are
called configurations. Restated, a configuration describes the
state of an atom by specifying the state of each individual electron
without specifying any relation between them. The energy
difference between configurations is usually very large. Therefore,
all other terms in the Hamiltonian are considered to be effective
only within a configuration.

II. 3 The Term

An approximation of the electron-electron electrostatic
interaction by a central-field potential led to a spherically
symmetric central-field potential for a full shell. We have
arrived at a consistent result for this configuration. However,
in the case of an incomplete shell, corrections must be
made to account for the non-central-field nature of the
electron-electron electrostatic interaction. This is done by
grouping together all the electrons in complete shells and
the nucleus into a "pseudo-nucleus" with a central potential
The interaction of the remaining electrons (not in full shells)
with the "pseudo-nucleus" and with each other is then con-
sidered. This is discussed in detail by Condon and Shortley.[22]
It is too involved to be repeated here.

The effect of the non-isotropic electrostatic field due
to incomplete shells is to split the configuration into terms.
It is recalled that the configuration was the classification of
an atomic state by the description of each electron in the atom.

---

[*] This is approximately true. Deviations from this rule cause
the rare earths to have incomplete shells.

It did not specify the orientations of the moments of one electron with respect to another. A term is an atomic state in which the relative orientations of the angular momenta of the electrons in a configuration are specified to give particular total moments. A term is a substate of a configuration. For example, the configuration $3d^2$ (two 3d electrons) can give rise to a total orbital moment which is any integer between 4 and 0. The total spin can be either 1 or 0. Specification of a particular possible value for each of the two momenta identifies a term. The lowest energy term is the term in which the total spin is the maximum allowed by Pauli's principle. Among terms with this maximum spin, the term with the largest total orbital moment consistent with Pauli's principle has the lowest energy. These results are also known as Hund's rules.

The terms are approximate eigenstates of the atom as long as the electron-electron interaction is stronger than the crystalline field or spin-orbit coupling. In the free atom, the generation of the terms is called Russel-Saunders coupling.

The energy difference between terms is, again, usually in the optical region. Bleaney and Stevens[17] adopt the approach in which this splitting is considered greater than that due to the crystalline field which follows. Mixing of terms due to the crystalline field is not considered. As we have mentioned before, this approximation is not very good. The alternate methods are discussed later in this chapter.

Following the Coulomb interaction, further perturbation and removal of degeneracy occur through the effects of the crystalline field and spin-orbit interaction. These two effects are not conveniently treated simultaneously. Therefore, it is necessary to determine which of the two effects are dominant. It has been determined that in the iron group, where

the incomplete shell is the outermost shell of the ion, the electrons
in the shell are sensitive to the crystalline field. The ionic eigen-
states in the crystalline field are considered as the basis upon which
the smaller spin orbit coupling are considered to act.

II. 4 The Effect of the Crystalline Field on the Orbital State

The crystalline field term in the Hamiltonian is due
to the interaction of the electrons in the iron group ion with the
electrostatic field of its charged neighbors. Strictly speaking,
it is the field due to all the other ions in the crystal. However,
it is often estimated by taking the nearest neighbors only.

Because the electrostatic field in question is the field
due to charges other than the field of the central ion, the field
at the central ion can be represented as a general solution to
Laplace's equation up to the radius of the nearest neighbor.

$$V = \sum_n \sum_{m=-n}^{+n} a_{n, m} r^n Y_n^m (\theta, \phi) \tag{2.3}$$

We are interested only in that part of V which interacts
with the orbital states of the central ion. Therefore, we can
neglect any term in V for which there exist no matrix elements
among the orbital states. That is, if

$$< a_i | r^n Y_n^m | a_j > = 0$$

for all i and j, the Y_n^m term in the potential is ignored.

The atomic orbital states to which this perturbing poten-
tial is applied are combinations of products of single electron
functions. Furthermore, as we have outlined in the previous
section, they are characterized by a particular value of total
orbital moment $\overline{L}$ and a particular $\overline{S}$, of the total spin.

A typical matrix element of V is of the form

$$\sum_k \int (\psi_k^{*'} \cdots \cdots \psi_2^{*'} \psi_1^{*'} V_n^m (\tau_k) \psi_1 \psi_2 \cdots \psi_k) d\tau_k$$

$$= \int \underline{\psi}^{*'} V_n^m \underline{\psi} d\tau \tag{2.4}$$

Each of the single electron functions ψ_k are spherical harmonics multiplied by a radial function. For the iron group, all the electrons are in the 3d shell. So we have n=2. The matrix elements are proportional to

$$\int |f(r)|^2 \cdot Y_2^{-m'} Y_n^\mu Y_2^m d\tau \tag{2.5}$$

From the properties of spherical harmonics we know that this integral is zero unless $n \leq 4 = 2l$ and $m' = \mu + m$. Furthermore, if ψ' and ψ are of the same orbital moment l, the product $\psi'\psi$ is an even function. Therefore, for the product $\psi'^* Y_n^\mu \psi$ to be non-zero, Y_n^μ must likewise be even. This limits the interest in n to just the even n's. For the rare earths, where $l = 3$, we must take all the even n's up to $2l = 6$. This greatly limits the terms in the crystalline field to be considered.

We can obtain further information about the general form of the crystalline field by consulting the crystallo- graphic data on the crystal in question. These sources provide all the relevant distances to locate the position of a particular atom in the lattice and the point symmetry about this position.

The crystalline field about an ion must have a form which is consistent with the point symmetry about the ion. If a p-fold rotational symmetry is present, the crystalline field can only contain terms Y_n^m, where m is restricted to multiples of p. If a horizontal reflection plane exists, the values of m must be even for the iron group; this is necessary because l is even. Many such relations serve to

greatly simplify the crystalline field. In fact, if the rotational symmetry about an ion is sufficiently high, the only relevant portion of the crystalline field is that of axial (cylindrical) symmetry. An iron group ion in a hexagonal site would be such an example.

After the simplest relevant form of the crystalline field is found, the orbital energies and eigenstates under its influence are calculated. Given the matrix elements of V, this can be carried exactly for many cases. In the cases of very low symmetry, the use of perturbation methods may be necessary.

The explicit calculation of the matrix elements can be made from (2.4). This is a fairly tedious process because $\bar{\psi}$ are anti-symmetric functions of many electrons. A method which greatly simplifies the calculation of the non-radial part has been provided by Stevens.[24] In this method, the crystalline field is replaced by an equivalent operator, which operates on the atomic orbital states $| L, M >$ instead of the individual electron orbital states. It is based on the proportionality which exists between the matrix elements of variables x, y and z as vector operators and the matrix elements of L_x, L_y, and L_z in a manifold of constant L. Tables giving the results of explicit calculations using this method are provided by Elliot and Stevens[25] for all the ions in the iron and rare-earth groups. The results are for spherical harmonics of unit amplitude. The actual field amplitude is required for the final evaluation of the matrix elements. In addition, it must be multiplied by the radial part of the matrix element,

$$\int f^2(r) r^{n+2} dr,$$

where f(r) is the radial part of the electronic orbital function. This is a factor which is not known to any accuracy. It is because of the unreliable nature of the values for both the

crystalline field strength and the function $f(r)$, that the energy levels in the crystalline field are measured by optical absorption instead of being calculated. However, the calculations do provide values of relative energies which are sufficiently reliable to determine which state is the ground state and the degeneracies of each level.

II. 5 The Effect of Spin-Orbit and Zeeman Energies, The Case of the Non-Degenerate Ground Orbital State

The final step in the determination of the lowest energy levels with the total Hamiltonian is the application of the spin-orbit coupling term and the Zeeman term in the Hamiltonian. The current approach to this problem is due to Abragam and Pryce,[26] who separated the problem into the case of the non-degenerate orbital ground state and the case where the orbital ground state is degenerate. We arrive at such ground states from the splitting of the term by the crystalline field as described in the preceding section.

In this case, the degeneracy which exists before the application of spin-orbit coupling and the Zeeman energy is just the degeneracy due to spin. This degeneracy is partially or completely removed by spin-orbit coupling and completely removed by the Zeeman energy, in any case. Abragam and Pryce have developed a spin-Hamiltonian which is a pure spin operator which is applied to the spin states. In such an operator, the orbital contribution through spin-orbit coupling and orbital Zeeman energy are contained in constant coefficients which can be evaluated by second-order perturbation because the orbital ground state is non-degenerate.

The spin-orbit and Zeeman energy are given by the following Hamiltonian:

$$\mathcal{H} = \lambda \overline{L} \cdot \overline{S} + \overline{H} \cdot \overline{L} + g\beta\overline{H} \cdot \overline{S} = \overline{L}(\lambda\overline{S} + \overline{H}) + g\beta\overline{H} \cdot \overline{S} \qquad (2.6)$$

If we consider just the spin states associated with the ground orbital state, the matrix elements are of the form

$$< 0, m'_s |\mathcal{H}| 0, m_s > , \text{ where } |0>$$

is the orbital ground state. For terms in the Hamiltonian involving $\overline{L}$, this means that the matrix elements will contain a factor $<0|\overline{L}|0>$. For non-degenerate orbital states, this is always zero. Therefore, the lowest spin states are independent of the effects of orbital moments. This is approximately true for large magnetic fields.

In the range of magnetic fields used for microwave paramagnetic resonance, this is usually a poor approximation. The reason for this is that the terms in the Hamiltonian involving L do have matrix elements connecting the ground orbital state to excited orbital states. This mixes a small amount of the excited state into the ground state, so that in the second-order approximation, the energy of the spin states becomes dependent on L. This dependence can be quite large compared to the Zeeman energy because the spin-orbit coupling constant is a fairly large constant.

The constant coefficients in the spin-Hamiltonian are related to the spin-orbit and orbital Zeeman energy by the second-order energy expression

$$E'' = \sum_k \frac{\left| \sum_i < k | L_i | 0 > (\lambda S_i + \beta H_i) \right|^2}{E_o - E_k} \qquad (i = x. \ y. \ z)$$

$$(2.7)$$

$$= \sum_{k, i, j} \frac{< k | L_i | 0 > < 0 | L_j | k >}{E_o - E_k} (\lambda^2 S_i S_j + 2 \lambda \beta H_i S_j + \beta^2 H_i H_j)$$

The total perturbed energy is then

$$(2.7) + g_e \beta \bar{H} \cdot \bar{S} \qquad (2.8)$$

which is usually rewritten

$$\mathcal{H}_{spin} = \beta \ \bar{H} \cdot \ g \cdot \ \bar{S} + \bar{S} \cdot \ D \cdot \ \bar{S}$$

where g and D are tensors. The quadratic term in H is disregarded because it is not a function of S. It cannot contribute to the splitting of spin states. By proper choice of axes, D and g can usually be diagonalized.

$$\mathcal{H}_{spin} = \beta \ (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z)$$
$$+ D_x S_x^2 + D_y S_y^2 + D_z S_z^2 \qquad (2.9)$$

Terms of higher power in S can be obtained by going to· expression for higher perturbed energy. However, we know in advance that the powers of H and S must always add up to an even number. This is necessary if the spin-Hamiltonian is to be invariant under time reversal.

In principle, the spin-Hamiltonian can be derived and the coefficients computed explicitly if the ground and excited orbital functions and their energies were known. In practice, we have only qualitative information about the orbital levels

and functions. Therefore, only the form of the Hamiltonian is chosen to fit the point-symmetry of the ion site and the coefficients determined by measurement.

In this spin-Hamiltonian, the dipole-dipole interaction between spins and the interaction of any nuclear magnetic moment with the spin and the orbit have been ignored. These factors were taken into account by Abragam and Pryce to give a complete spin-Hamiltonian of the following form:

$$\mathcal{H}_s = \bar{S} \cdot D \cdot \bar{S} + \beta \bar{H} \cdot g \cdot \bar{S} + \bar{S} \cdot A \cdot \bar{I} + \bar{I} \cdot P \cdot \bar{I} - \gamma \beta_N \bar{H} \cdot \bar{I}$$

$$(2.10)$$

where g, D and A are tensors of rank 2, $\bar{I}$ is the nuclear spin.

The spin-Hamiltonian appropriate to various common symmetry are given below.

Trigonal

$$\mathcal{H}_s = \beta (g_{||} H_x S_z + g_\perp H_x S_x + g_\perp H_y S_y) + DS_z^2 + \frac{35F}{180}(S_z^4 - \frac{6}{7}S(S+1)$$

$$\cdot S_z^2 + \frac{5}{7}S_z^2) + \frac{a}{6}(S_x^4 + S_y^4 + S_z^4)$$

$$= \beta (g_{||} H_z S_z + g_\perp (H_s S_x + H_y S_y)) + DS_z^2 + \frac{7}{36}(F-a)$$

$$\cdot [S_z^4 - \frac{6}{7}S(S+1)S_z^2 + \frac{5}{7}S_z^2] - \frac{\sqrt{50}}{180}a[S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z]$$

Orthorhombic

$$\mathcal{H}_s = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D_x S_x^2 + D_y S_y^2 + D_z S_z^2$$

$$= \qquad '' \qquad + D_z' S_z^2 + E(S_x^2 - S_y^2)$$

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Tetragonal

$$\mathcal{H}_s = \beta\left[g_{11}H_z S_z + g_\perp(H_s S_x + H_y S_y)\right] + DS_z^2 + \frac{7F}{36}\left[S_z^4 - \frac{6}{7}S(S+1)S_z^2 + \frac{5}{7}S_z^2\right]$$

$$+ \frac{a}{6}(S_x^4 + S_y^4 + S_z^4)$$

Cubic

$$\mathcal{H}_s = g\beta\overline{H}\cdot\overline{S} + \frac{a}{6}(S_x^4 + S_y^4 + S_z^4)$$

One additional simplification can be made in many cases of high symmetry. This is due to the limited freedom of response of small spin manifolds to their environment. A spin of $\frac{1}{2}$ can have only two orientations: up or down. But the even parity of all spin-Hamiltonian always makes these two directions equivalent. The only distinction which such a limited spin manifold can make is a difference in the elements of the g-tensor.

A spin of 1 can distinguish a monoclinic symmetry but no more. A symmetry which is higher can be represented only by an axially symmetric or spherically symmetric spin-Hamiltonian with the exception of the g-tensor. A spin of 3/2 can distinguish a symmetry as high as orthorhombic; higher symmetries can be represented by an axial or spherical Hamiltonian except for the g-tensor. A spin of 2 can distinguish symmetries up to and including trigonal symmetry. Finally, a spin of 5/2 is capable of distinguishing any symmetry representable by spherical harmonics of order 4.

For ions of iron group, it is found that the crystalline field about the ion is almost always approximately cubic. The reason for this lies in the ratio of ionic radii of iron group ions to common anion neighbors, particularly oxygen. Relatively small distortions from cubic symmetry are in the form of distortions along one or more axes of the cube producing tetragonal or orthorhombic symmetry or a distortion

along a body diagonal to produce trigonal symmetry. The spin-Hamiltonian then takes a cubic form with terms of lower symmetry added. When these terms are of sufficiently low symmetry, such that they can be expressed in spherical harmonics of the order 2, they take on a relative magnitude disproportionately large compared to the cubic part of the spin-Hamiltonian. This is because terms in the spin-Hamiltonian which are equivalent to spherical harmonics of order 2 are the result of second-order perturbation; whereas, the cubic part must be the result of fourth order perturbation. Thus, a small quadratic term in the crystalline field can produce a coefficient in the spin-Hamiltonian which is much larger than that produced by a large cubic potential. Thus, except for very exceptional cases, the quadratic terms in the spin-Hamiltonian are, by far, the most important ones when they exist. We can discuss the qualitative behavior of the spin under the spin-Hamiltonian by just taking the quadratic terms whenever the symmetry is non-cubic.

II.6 Zero-Field Splitting

One of the very important features of the spin-Hamiltonian is that the degeneracy of the spin states is partially removed even in the absence of a magnetic field. Taking the simple, axially symmetric Hamiltonian as an example, we have

$$\mathcal{H}_s = \vec{S} \cdot D \cdot \vec{S} = DS_z^2$$

This Hamiltonian splits the spin states into levels given by $\epsilon = Dm_z^2$, where m_z is the z-component of the spin moment. This gives levels determined by $|m_z|$ and results in doubly degenerate levels $(+m_z, -m_z)$ except for the state $m_z = 0$. If the number of electrons is odd so that the spin is half-integral, all the levels become doubly degenerate. Kramer[27] has proved

that this must always occur for an odd number of electrons regardless of the symmetry.

In an orthorhombic symmetry, for example, the spin-Hamiltonian is

$$DS_z^2 + E(S_x^2 - S_y^2) = DS_z^2 + E/2(S_+^2 + S_-^2),$$

where,

$$S_+ = S_x + iS_y \text{ and } S_- = S_x - iS_y.$$

This Hamiltonian mixes states $m_s \pm 2$ with the state m_s. For $S = 3/2$, we obtain two levels both doubly degenerate. The matrix of $\mathcal{H}_s$ is

	+3/2	-1/2	-3/2	+1/2
3/2	9D/4	$\sqrt{3E}$	0	0
-1/2	$\sqrt{3E}$	D/4	0	0
-3/2	0	-	9D/4	$\sqrt{3E}$
+1/2	0	0	$\sqrt{3E}$	D/4

The energies are solutions to the secular equation

$$(\frac{9}{4}D - \epsilon)(\frac{D}{4} - \epsilon) - 3E^2 = 0$$

$$\frac{9}{16}D^2 - \frac{10}{4}D\epsilon + \epsilon^2 - 3E^2 = 0 \qquad (2.11)$$

They are

$$\epsilon = \frac{\frac{10}{4}D \pm \sqrt{(\frac{5D}{2})^2 - 4(\frac{9}{16}D^2 - 3E^2)}}{2}$$

$$= \frac{5}{4}D \pm \sqrt{D^2 + 3E^2}$$

The spin states are obtained by substitution of back into the secular equation. They are

$$\sqrt{\frac{\sqrt{D^2+3E^2}-D}{2\sqrt{D^2+3E^2}}}\,|\pm\tfrac{3}{2}> - \sqrt{\frac{3E^2}{2(D^2+3E^2-2\sqrt{D^2+3E^2})}}\,|\pm\tfrac{1}{2}>$$

$$= A|\pm\tfrac{3}{2}> - B|\mp\tfrac{1}{2}>$$

and

$$B|\pm\tfrac{3}{2}> - A|\mp\tfrac{1}{2}> \tag{2.12}$$

for the upper and lower energies, respectively.

The physical reason for this energy splitting in zero field is as follows. A stationary electrostatic field locks the electrons inthe lowest energy position. If there is only one such position, the electrons are stationary and lose their orbital moment. Spin-orbit coupling re-induces a small amount of orbital moment which, in the second-order perturbation, reduces the energy by the spin-orbit energy. If the ion were situated in an isotropic environment, the amount of induced orbital moment and the resulting spin-orbit energy would be equal for all orientations of spin. Thus, we would have no zero-field splitting. If the environment is anisotropic, the amount of induced orbital moment can differ for different orientations of the spin. This results in zero-field splitting. Because of the magnitude of the spin-orbit coupling constant (~ 100 cm.$^{-1}$), only a small difference in orbital moment can result in zero-field splitting in the range of a microwave quantum.

II. 7 The Zeeman Energy

The energy which a magnetic moment acquires in a magnetic field is called the Zeeman energy. because of the quantization of the magnetic moment in the direction of the applied field, $2J+1$ discrete levels result from the application of the magnetic field. It is represented in the spin-Hamiltonian by the term,

$$\beta \overline{H} \cdot g \cdot \overline{S}$$

If the coordinates are chosen properly with respect to the crystalline field, the g-tensor is usually diagonal. In this case

$$\beta \overline{H} \cdot g \cdot \overline{S} = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z)$$

For a pure spin state $g_x = g_y = g_z = 2.003$. Thus, we have

$$\beta \overline{H} \cdot g \cdot \overline{S} = g\beta \overline{H} \cdot \overline{S}.$$

In the spin-Hamiltonian, the small orbital component in the magnetic moment causes g to deviate from the pure spin value. Mathematically, this is due to the cross-terms between H and S in the second-order perturbed energy expression used in the derivation of the spin-Hamiltonian.

$$\sum_k \frac{\left| \sum_i < 0 | L_i | k > (\lambda S_i + \beta H_i) \right|^2}{E_o - E_k}$$

which gives for the coefficient of the terms $\beta H_i S_i$,

$$\sum_k \frac{| < 0 | L_i | k > |^2}{E_o - E_k} \cdot 2\lambda$$

This quantity is added to 2.003 to form g.

Physically, this quantity can be explained in the following way. To first approximation, the orbital moment is zero. The presence of spin and the application of a magnetic field both serve to induce a small amount of orbital moment

by mixing excited orbital states. The spin interacting with orbital moment induced by itself gives zero-field splitting. The spin interacting with the orbital moment induced by the applied magnetic field contributes to g. Similarly, the magnetic field interacting with the orbital moment induced by the spin contributes an equal amount to g. In fact, the deviation of g from 2.003 is a direct measure of the induced orbital moment.

$$L_i = \frac{(g - 2.003)}{2} \cdot (\lambda S + \beta H)$$

The close relation between zero-field splitting and the deviation of g from 2.003 has been pointed out by Bleaney and Stevens.[16] Namely,

$$\frac{(g_i - 2.003)}{2} \lambda = D_i$$

λ is of the order of 100 cm^{-1}. This shows that a deviation of g from 2.003 of .01 can cause a zero-field splitting up to .5 cm^{-1}. The zero-field splitting is due to the difference in D in different directions. Therefore, it can be expected to be somewhat smaller unless the D_i are of different signs.

In ions where the ground term in the configuration has no angular momentum the physical basis for the spin-Hamiltonian is quite different, and these relations may not hold.

II. 8 Hyperfine Structure

The term $\bar{S} \cdot A \cdot \bar{I}$ in the spin-Hamiltonian represents the interaction of the nuclear magnetic moment (spin) of the paramagnetic ion with its electrons. This is a static dipole-dipole interaction which is governed by the relative orientations and positions of the two moments.

The effect is to split each electronic spin level into $2I+1$ levels, the spacing between the new levels being proportional to the value M_s of the spin state. As the result, each allowed spin transition, $\Delta m = \pm 1$, is now split into $2I+1$ separate transitions. The transitions are equally spaced in frequency with

$$\Delta f = A$$

when A is expressed in frequency. This group of $2I+1$ lines is called the hyperfine structure of a line. This is illustrated for the simple case of $\vec{S} \cdot A \cdot \vec{I} = A \cdot \vec{S} \cdot \vec{I}$, S=2 and I=1 in Fig. 2.

When A is large compared to the width of the line, the $2I+1$ lines are distinct. They are easily indentified by their equal intensities and equal spacings. This provides one way for the identification of paramagnetic ions which possess known nuclear spin. When A is small compared to the line width, it simply contributes to the line width as inhomogenous broadening.

Interaction with the nuclear moments of neighboring nuclei is also present when such moments exist. This causes additional splitting of the resonance line. The splitting is naturally small and consists of a great many lines. Tinkham[28] was able to resolve these lines in the resonance of iron group impurities in ZnF_2. More often, these lines are not resolved and contribute to the line width as inhomogeneous broadening.

II. 9   The Case of the Degenerate Orbital Ground State

When the ground orbital state is degenerate before the consideration of spin-orbit coupling, the spin-Hamiltonian, which was based on a second-order perturbation of the orbital state, is no longer valid. Spin-orbit coupling will completely mix the degerate orbital states. The qigenstates must be obtained by exact diagonalization of the spin-orbit matrix.
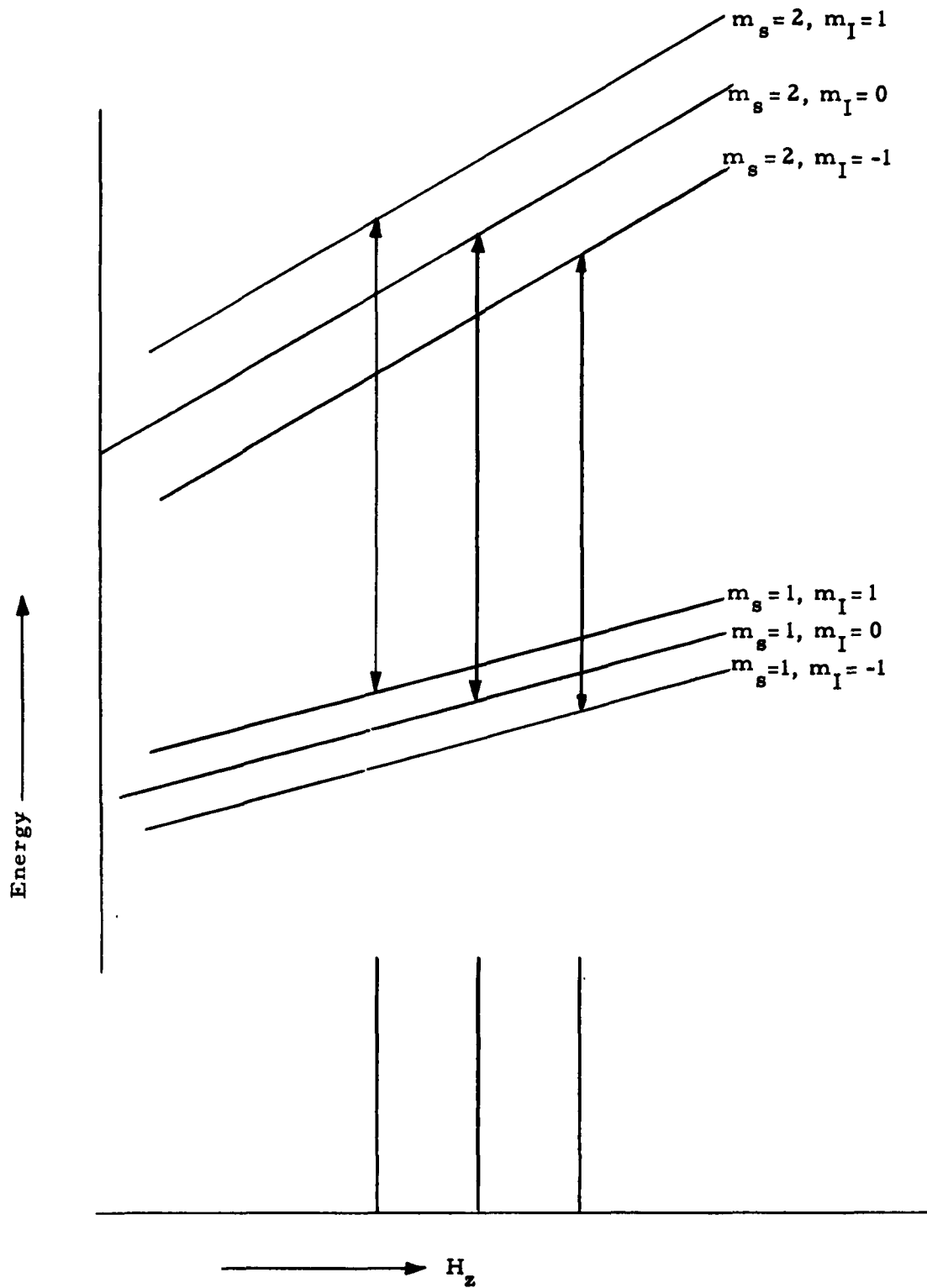
Hyperfine Spectrum.

Figure 2

The liberal mixing of the orbital states generally results in a large orbital moment. This has the following effect of the paramagnetic behavior of the ion:

(a) The value of g deviates considerably from 2.

(b) The zero-field splitting becomes very large, usually beyond the microwave range.

(c) The relaxation time T_1 becomes very short.

The last two effects make this case unfit for maser applications.

There is, however, one special case where, in spite of an orbital degeneracy, the orbital moment is small. This is the case of Cr^{2+} in an octahedral (6-coordination cubic) field, Fe^{2+} in a cubic (8-coordination cubic) field, and Cu^{2+} in an octahedral field.[*] These orbital ground states are doubly degenerate but have the special property that they are non-magnetic.[29] That is, the matrix of $\bar{L}$ is identically zero within the doublet. When the field is not strictly cubic, the states become weakly magnetic, and the degeneracy is removed except in the case of trigonal symmetry. Cr^{+2} in the rhombic field of $CrSO_4 \cdot 5H_2O$ was found to have a g of 1.95 for $g_{\parallel}$ and 1.99 for $g_\perp$.[30]

In a trigonal symmetry, the states remain degeneracy but acquire a magnetic moment L_z in proportion to the amount of the trigonal distortion. In this case, it is speculated that a distortion of the symmetry takes place, which removes the degeneracy and lowers the energy of one of the states. This is called the Jahn-Teller effect.[31] The effect was originally proposed for molecular complexes. However, it has been applied to iron group ions in hydrated salts by Van Vleck.[32] Bleaney et al.[33] have observed a spectrum of Cu^{2+} at low

[*] The 6-coordination cubic and 8-coordination cubic have the same form of field when expressed in spherical harmonics, but the polarity is reversed. Thus, the lowest levels in one become the highest levels in the other.

temperature which could be explained by the Jahn-Teller effect.

The case of Cu^{2+} in the hydrated salts of trigonal symmetry (fluosilicates, etc.) is explained in the following manner. The degeneracy in the trigonal field is removed by a Jahn-Teller distortion. But the lowest orbital state has three equivalent orientations so that three separate spectra are observed. At high temperature, these orientations become mixed, and the spectrum becomes isotropic. (The spectrum of Cu^{2+} in a trigonal field would be almost isotropic if the orbital ground state were non-degenerate.)

II.10 Other Methods for the Analysis of Paramagnetic Ions

The spin-Hamiltonian of Abragam and Pryce[26] was based on a perturbation calculation in which the crystalline field is weaker than the electrostatic force between the electrons in the ion but stronger than the spin-orbit coupling. This made the ground term in the configuration the starting point in the calculation.

The spin-Hamiltonian is explained in another way by Bowers and Owens[20] in their review of paramagnetic resonance. Their starting point is the configuration. The crystal field acts on each electron in the configuration, splitting the orbital degeneracy of the single electrons. If n electrons of the same shell form the configuration, the electrons are assigned to occupy the n lowest energy orbitals of an isolated electron in the crystal field. This forms the ground state. The proper degeneracy in the orbital ground state is obtained this way. The form of the Hamiltonian was obtained only from the knowledge of the ground orbital state degeneracy and the crystalline field symmetry. Therefore, either method yields the same result. To the inexperienced researcher, it is somewhat

surprising that the second approach, which ignores the electrostatic repulsion between the magnetic electrons, gives the proper ground state.

In optical work, however, the approach of Bowers and Owens is the accepted one. This is known as the crystalline field approximation because it assumes that the crystalline field is dominant over the electron-electron electrostatic field. The reason for this difference in approach is that, as far as the ground orbital state is concerned, the Russel-Saunders[22] approach is good. However, the higher energy levels of the ground term in the crystalline field approach the lowest levels of the next highest term, and considerable mixing occurs. The Russel-Saunders coupling is no longer accurate. Thus, for optical work it is a poor approximation.

Some light is shed on this problem by the recent work of Racah, Low et al.[23] They have undertaken a project of finding the energy levels and states of iron group and rare-earth ions in a cubic field. It is to be extended to lower symmetries. They have found, by use of a computer, the exact levels and states starting from the LSJM representation. This is a representation in which the spin-orbit coupling is diagonal. Although the crystalline field is stronger than the spin-orbit coupling, this introduces no inaccuracy because the computer solves the problem exactly without resorting to perturbation methods. All the terms in the configuration with the ground S-state are used.

The result shows that the ground orbital state is very nearly the state given by the Russel-Saunders coupling. Most of the excited states cannot be represented even approximately by the Russel-Saunders coupling.

II. 11 Koster's Method

Koster[19, 34] has developed a group-theoretical method by which the number of independent terms required in a complete spin-Hamiltonian is given.

In this approach, it is assumed that the eigenstates and energies for the complete Hamiltonian, in the absence of a magnetic field, is solved. This includes all the terms in the complete Hamiltonian including the crystalline field and spin-orbit coupling. The Zeeman energy term is then applied as a perturbation. This method predicted many more independent terms than those included in the spin-Hamiltonian by Abragam and Pryce. For example, for $S = 3/2$, the spin-Hamiltonian of Abragam and Pryce terminates with terms in S_i^2. Koster's method includes the terms $H_i S_i^3$.

We note that such terms are allowed by the time-reversal symmetry of the spin-Hamiltonian. In fact, they would have appeared in the original Hamiltonian if the perturbation were carried out to the fourth order. But so would a number of other terms of the form $H^2 S^2$ and $H^3 S$. Why are these terms not predicted in Koster's complete spin-Hamiltonian?

The reason lies in the fact that Koster's method still had to resort to the perturbation method for the final step. It is a first-order perturbation expression. Higher order perturbation is necessary to produce terms of higher power in H. Physically, omission of higher order perturbation in the orbital Zeeman energy means that the induction of orbital moment by the magnetic field is ignored. This is actually a very good approximation. The spin-orbit energy, which is the next least powerful term in the total Hamiltonian, is at least 100 times stronger than the orbital Zeeman term at practical magnetic fields.

Experimental evidence of the additional energy terms predicted by Koster has been reported.[35] The effect is small. It appears that in most cases they can be neglected.

II, 12 The Theory of T_1

When the spin system is not in thermal equilibrium with a thermal bath with which it is in contact, it will relax into equilibrium in a characteristic time T_1 in the absence of a driving source. The relaxation time T_1 is a measure of the contact (or lack of contact) with the thermal bath.

The problem of spin relaxation has been studied by Van Vleck.[36] His results were not completely satisfactory, but the approach is generally accepted. The principles of his theory are reviewed here. Mattuck and Strandberg[79] have restudied the problem and have arrived at substantially the same results.

Quantum mechanically, thermal spin relaxation is treated as the transition between spin-states under the excitation due to the thermal bath (in this case, the lattice). The transition rate is the reciprocal of T_1.

Spins can interact only with magnetic fields. The lattice, on the other hand, is non-magnetic. Therefore, to first order, there is no thermal contact and T_1 is infinite. However, a contact of the second order does exist. In this process, the time-varying electric field, due to the thermal vibration of the lattice, interacts with the electrons in the paramagnetic ion. This affects the orbital moment of the ion which, in turn, interacts with the spin to induce the required transition.

The total Hamiltonian for the spin and lattice in mutual contact is

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_L + \mathcal{H}_z + \mathcal{H}_{S0} + \mathcal{H}_{0L} + \mathcal{H}_{SS} \tag{2.13}$$

H_0 is the energy of the orbital state in the crystalline field without the spin-orbit coupling, H_L is the energy of the lattice vibrations, H_z is the Zeeman energy, H_{SO} is the spin-orbit energy, H_{OL} is the orbit-lattice coupling energy, and H_{SS} is the spin-spin interaction which introduces line width. $H_0 + H_L$ is taken as the unperturbed Hamiltonian, and the remainder is the perturbing Hamiltonian. It acts on the manifold of eigenstates of H_0 and H_L.

The transition from the spin state $| + >$ to $| - >$ is computed by using a "new" effective Hamiltonian.

$$H_{new}(ii') = \sum_{j, k} \frac{[H'(ij)H'(j, k)H'(k, i')]}{h\nu(ij)h\nu(jk)} \qquad (2.14)$$

The indices, i, j, k and i' designate compound states of spin, orbit and lattice. i and i' designate the ground orbital state with spin states $| - >$ and $| + >$, respectively.

The matrix element H'(ij) is a sum

$$H'(ij) = H_{SO}(ij) + H_{OL}(ij) + H_z(ij) + H_{SS}(ij) \qquad (2.15)$$

When the ground orbital state is a singlet, $H_{SO}(ij)$ and $H_{OL}(ij)$ are zero whenever j contains the orbital ground state. Therefore, the sum over j and k are over states containing only excited states. When Eq. (2.15) is substituted into Eq. (2.14) among the products we find

$$\frac{H_{SO}(p + n_i, q - n_i)H_{SO}(q-n_i, r-n_i)H_{OL}(r-n_i, p-n_i+1)}{[E(p) - E(q)][E(q) - E(r)]} \qquad (2.16)$$

and all the permutations thereof. Such terms represent third order transitions from the state $| + >$ to $| - >$. At the same time, the lattice state changes from n_i to $n_i + 1$. The spin and the lattice exchange energy. Second order terms cancel out almost completely.

The transition probability is proportional to the square of $H_{new}(i\,i')$. It can be seen from (2.16) that the probability is proportional to $\frac{\lambda^4}{\Delta^4}$. λ is the spin orbit coupling and Δ is the energy separation between the orbital levels in a crystalline field. These separations are not equal by any means, but for a qualitative discussion, they are all equated to a single Δ.

The factor $\frac{\lambda}{\Delta}$ was previously encountered in the derivation of the spin-Hamiltonian. It represents an orbital moment induced by spin-orbit coupling in an otherwise "quenched" state. It was responsible for zero-field splitting and the deviation of g from 2. In fact, the deviation of g from 2 was given by $\frac{\lambda}{\Delta}$. Therefore, the g-factor is a convenient index by which relative relaxation times can be estimated. A long relaxation time is incompatible with a large deviation of g from 2.

The strength of the crystalline field enters into T_1 in two ways. Δ is proportional to the strength and so is H_{0L}. Since $\frac{1}{T_1}$ or the transition probability is proportional to

$$\frac{H_{0L}^2}{\Delta^4} ,$$

it appears that a strong field results in a longer relaxation time. The quartic dependence of the transition probability on λ indicates that a very large variation of T_1 is expected in the iron group. V^{2+} has a λ of $55\,cm^{-1}$ while Cu^{2+} has $-852\,cm^{-1}$. This would indicate a ratio of relaxation times of the order of $(15)^4 \sim 50,000$.

CHAPTER III

THE RELATIONSHIP BETWEEN THE MATERIAL
PARAMETERS AND MASER PERFORMANCE

III. 1 Bloch's Equations

A brief review is made of the two-level maser to show
the relation between parameters of the maser material and the
maser performance. This relation is valid also for three-level
masers with only a simple correction.

We have a paramagnetic solid containing N particles per
unit volume, each with a spin of 1/2. In the presence of a mag-
netic field, the spin state $m_s = 1/2$ will have an energy $2\beta H_o$
higher than the state $m_s = -1/2$. Here β is the Bohr magneton,
and H_o is the dc magnetic field. Boltzmann's distribution
gives a population of the lower state which is larger than the
population of the higher state by

$$\Delta N = N_o \frac{1 - l^{-\Delta E/KT}}{1 + l^{-\Delta E/KT}} \qquad (3.1)$$

where K is Boltzmann's constant, and T is the temperature in
Kelvin. If $\Delta E << KT$, $\Delta N \approx N_o \frac{\Delta T}{2KT}$. We have as the result
a net induced magnetic moment which we shall call

$$\mu_o = \beta \Delta N = \beta N_o \frac{\Delta E}{2KT}$$

The net angular momentum in units of $\hbar$ is $\frac{\Delta N}{2} = M_o$. The
analysis of a maser can be made while restricting our-
selves to M_o because the remainder of the spins will always
cancel itself out.

The behavior of the net moment M_o under a time-
varying magnetic field excitation was analyzed by Bloch[37]

in connection with nuclear magnetic resonance. The treatment was made by the now famous Bloch equations. These are classical equations. However, they give results which are in perfect agreement with experiments and with quantum mechanical analysis for the simple cases where quantum mechanical analysis is possible. In addition, relaxation effects can be included in a simple way; whereas, in a quantum mechanical treatment it is extremely complex.

The equations are basically the equations of the spinning top.

$$\frac{d\overline{M}}{dt} = T \text{ (torque)} = \gamma \overline{M} X \overline{H} \tag{3.2}$$

γ is the ratio of magnetic moment to the mechanical angular momentum. (For an electron this is $\frac{2\beta}{\hbar} = .927 \times 10^{7}$.) Here, H is the total magnetic field. Equation (3.2) can be written for a rectangular coordinate system rotating about the z-axis with an angular velocity $\overline{\omega}$.

$$\frac{dM}{dt} = -\overline{\omega} X \overline{M} + \gamma \overline{M} X \overline{H} = \overline{M} X (\gamma \overline{H} + \overline{\omega}) \tag{3.3}$$

where H is now

$$\overline{a}_z [\overline{H}_o + H^2_{r.f.} \cos \omega t] + \overline{a}_x [\frac{H^{\perp}_{r.r}}{2} \cos 2\omega t + \frac{H^{\perp}_{r.f.}}{2}] + \overline{a}_y [-\frac{H^{\perp}_{r.f.}}{2} \sin 2\omega t]$$

The three components of this equation are

$$\frac{dM_x}{dt} = M_y [\gamma(H_o + H^2_{r.f.} \cos \omega t) + \omega] + M_z \cdot \frac{\gamma H^{\perp}_{r.f.}}{2} \sin 2\omega t$$

$$\frac{dM_y}{dt} = M_z [\gamma(\frac{H^{\perp}_{r.f.}}{2} + \frac{H^{\perp}_{r.f.}}{2} \cos 2\omega t)] - M_x [\gamma(H^2_o + H^2_{r.f.} \cos \omega t) + \omega]$$

$$\frac{dM_z}{dt} = -M_x \cdot \frac{\gamma H^{\perp}_{r.f.}}{2} \sin 2\omega t - M_y [\frac{\gamma}{2}(H^{\perp}_{r.f.} + H^{\perp}_{r.f.} \cos 2\omega t)]$$

As it stands, these equations are very difficult to solve. A very large simplification is made by ignoring the terms which are time varying. This would be justified if the resulting solution turns out to be a slowly varying function compared to the terms which were ignored.

The simplified equations are

$$\frac{dM_x}{dt} = M_y(\gamma H_o + \omega)$$

$$\frac{dM_y}{dt} = M_z \cdot \gamma \frac{H_{r.f.}^{\perp}}{2} - M_x'(\gamma H_o + \omega) \qquad (3.4)$$

$$\frac{dM_z}{dt} = -M_y \gamma \frac{H_{r.f.}^{\perp}}{2}$$

The solutions are

$$M_y = \frac{M_o \gamma H_{r.f.}}{2[Q]^{1/2}} \sin Q^{1/2} t$$

$$M_x = \frac{M_o \gamma H_{r.f.} (\gamma H_o + \omega)}{2Q} (1 - \cos Q^{1/2} t) \qquad (3.5)$$

$$M_z = \frac{M_o}{Q} \left[\frac{\gamma^2 H_{r.f.}^{\perp 2}}{4} \cos Q^{1/2} t + \frac{(\gamma H_o + \omega)^2}{Q} \right]$$

where $Q = \frac{\gamma^2 H_{r.f.}^{\perp}}{4} + (\gamma H_o + \omega)^2$

In the special case of $\gamma H_o + \omega = 0$,

$$M_x = 0 \text{ and}$$

$$M_z = M_o \cos \gamma \frac{H_{r.f.}^{\perp}}{2} t \qquad (3.6)$$

$$M_y = M_o \sin \gamma \frac{H_{r.f.}}{2} t$$

This shows that M_o rotates about the x-axis with an angular velocity

$$\omega' = \frac{\gamma H_{r.f.}}{2} \qquad (3.7)$$

Noting that only one circularly polarized component of $H_{r.f.}$ remains in the solution, we can call it H' to simplify the expressions.

$$\omega' = \gamma H' \qquad (3.8)$$

This is just a free precession of M_o about the rotating field H'. This condition is referred to as magnetic resonance.

The equation and solution just given do not include relaxation effects. Bloch took relaxation into account by inserting two damping times T_1 and T_2 in the following manner.

$$\frac{dM_x}{dt} = M_y(\gamma H_o + \omega) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = M_z \cdot \gamma H' - M_x(\gamma H_o + \omega) - \frac{M_y}{T_2} \qquad (3.9)$$

$$\frac{dM_z}{dt} = -M_y \gamma H' - \frac{(M_z - M_o)}{T_1}$$

H' is the circularly polarized component of $H_{r.f.}$ rotating at an angular frequency $+\omega$ about the z-axis.

These relaxation times are necessary for the following reasons. First, there is a continuous drainage of energy from the spin system by whatever mechanisms which exist that are trying to bring the spins into thermal equilibrium. The energy of the spin system is proportional to $-M_z$ when the d. c. magnetic field is in the z-direction. Therefore, a time constant T_1 is inserted to point M_z towards its thermal equilibrium value M_o. Secondly, the net spin moment M_o is not a single moment but is composed of many spins oriented in the same

direction. This orientation is imposed by the Boltzmann's distribution when the M_o is in the z-direction. But when M_o is in the x-y plane, it should relax towards the thermal equilibrium value for this direction which is zero. In addition, the dipole-dipole interaction between the component spins try to destroy M_o. Thus, for transverse components of M, Bloch added a damping term

$$-\frac{ML}{T_2}, \text{ where } T_2 \leq T_1.$$

The solution to Bloch's equation with relaxation is very involved for transient cases. The steady state solution is very easy to obtain. It is

$$M_z = \frac{[(\gamma H_o + \omega)^2 + \frac{1}{T_2^2}]\frac{M_o}{T_1}}{\frac{(\gamma H_o + \omega)^2}{T_1} + \frac{\gamma^2 H'^2}{T_2} + \frac{1}{T_1 T_2^2}} \qquad (3.10)$$

$$M_y = \frac{\gamma H' M_o(\gamma H_o + \omega)}{T_2[\gamma H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T}]}$$

$$M_x = \frac{\gamma H' M_o(\gamma H_o + \omega)}{[(\gamma H_o + \omega)^2 + \gamma^2 H'^2 + \frac{1}{T_2^2}]}$$

at resonance $\gamma H_o + \omega = 0$. Then

$$M_x = 0$$

$$M_y = \frac{\gamma H' M_o T_2}{1 + \gamma^2 H'^2 T_1 T_2} \qquad (3.11)$$

$$M_z = \frac{M_o}{1 + \gamma^2 H'^2 T_1 T_2}$$

If T_1 were infinite, $M_x = M_y = M_z = 0$. When T_1 is finite, as it always is, M_y and M_z become non-zero. Physically, it is easy to see why M_y must not be zero. A finite T_1 means that losses are present. It indicates the presence of a damping force on $\bar{M}$. In a steady-state condition, an equal and opposite force must exist which balances out the damping force. This is provided by $\bar{M} \times \bar{H} = H_x \cdot M_y$. For any transfer of energy to take place in the total spin system, some transverse M must be preserved even when T_2 is present. The non-zero value of M_z represents the extent to which the damping forces $\bar{M}$ towards its thermal equilibrium value.

The amount of energy absorbed by the spin system from the resonant magnetic field can be computed by simply equating it to the loss in the system.

$$P = -\left(\frac{M_z - M_o}{T_1}\right) 2\beta H_o = \text{rate of energy loss due to } T_1.$$

$$P = \frac{-\gamma^2 H'^2 M_o 2\beta H_o}{T_2} \frac{1}{[(\gamma H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}]} \qquad (3.12)$$

The results of Bloch's equations can also be expressed in terms of susceptibilities.

$$x = \frac{\mu}{H} = \frac{2\beta \; M}{H}$$

$$x_{DC} = 2\beta \; \frac{M_o}{H_o}$$

$$x'_{r.f.} = 2\beta \; \frac{M_x}{H_x} = 0$$

(3.13)

$$x''_{r.f.} = 2\beta \; \frac{M_x}{H_x} = \frac{\gamma \; M_o \cdot 2\beta}{T_2 \; (\gamma \; H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \; \frac{T_1}{T_2}}$$

When the standard phaser notation is used for the time-varying quantities, the susceptibility can be represented as a complex quantity. $x = (x' + jx'')$, where x'' is a negative because γ is negative. In terms of the susceptibility, $P = -\frac{1}{2}\omega x'' H'^2$.

The solutions to Bloch's equation have certain weaknesses. One is that the equations do not allow for the maintenance of a transverse moment. This was pointed out by Redfield.[38] The preservation of transverse moments for times up to T_1 has been demonstrated experimentally.[39] This is of some consequence in transient behavior when large differences exist between T_1 and T_2 but cause no difficulty in steady-state electron resonance. Another difficulty is that the power absorption pattern, as a function of frequency which is referred to as "line shape," is always Lorentzian with the Bloch equations. Experimentally, it is not always Lorentzian.

The value of x'' obtained by Bloch's equation is independent of the magnitude of the individual moments which make up the total moment. This is an expected weakness of a classical treatment. The proper dependence can be found by a simple quantum-mechanical treatment omitting explicit relaxation effects.

From the Bloch's equation we had

$$P = -2\omega''H'^2 = -\frac{1}{2}\omega x'' H_x^2$$

where H' was one circularly polarized component of H_x. Therefore,

$H_x = 2H'$. We can consider this to be the definition x''. The same power P can be written

$$P = (\text{number of transitions})(\text{energy of each transition})$$
$$\times (\text{rate of each transition}) = \Delta N \cdot \Delta E \cdot A$$

where A is the transition probability of a single ion. The quantum mechanical transition probability is given by

$$A = \frac{2\pi}{\hbar} \rho(k) \left| H_{kn} \right|^2$$

where H_{kn} is the matrix element of the perturbing Hamiltonian which induces the transition between states ψ_k and ψ_n, and $\rho(k)$ is the denstiy of states $\frac{dN}{dE_k}$. If the density is given as $\frac{dN}{d\omega_k}$, then

$$A = \frac{2\pi}{\hbar^2} \rho(\omega) \left| H_{kn} \right|^2$$

For a perturbing Hamiltonian $g\beta H_x \cdot S_x$

$$\left| H_{kn} \right|^2 = g^2 \beta^2 \left| \langle k | H_x S_x | n \rangle \right|^2$$

If the spin states are pure, only one component of H_x, namely H' contributes to the transition, giving

$$\left| H_{kn} \right|^2 = (g^2 \beta^2 H'^2/4) \left| \langle k | S_\pm | n \rangle \right|^2$$

$\rho(\omega)$ can be interpreted as the line broadening. We can identify this with

$$\frac{1}{\pi T_2 [\ (\gamma H_0 + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}\ ]}$$

which we found in the solution to Bloch's equations. If A
represents the transition probability of one ion, then $\rho(\omega)$
must be normalized so that

$$\int_{-\infty}^{\infty} \rho(\omega)d\omega = 1.$$

Integration of the line-shape factor

$$\frac{1}{T_2[(\gamma H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}]}$$

shows it to be π. Therefore,

$$\rho(\omega) = \frac{1}{\pi T_2[(\gamma H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}]}$$

Substitution into P gives

$$P = \Delta N \cdot \Delta E \cdot \frac{2\pi}{\hbar^2} \cdot \frac{1}{\pi} \cdot \frac{g^2\beta^2 H'^2 |<k|S_{\pm}|n>|^2}{T_2[(\gamma H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}]}$$

$$= \frac{2\Delta N \cdot \omega}{\hbar} g^2\beta^2 H'^2 \frac{|<k|S_{\pm}|n>|^2}{T_2[(\gamma H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}]}$$

$$\chi'' = \frac{\Delta N g^2 \beta^2}{\hbar} \frac{|<k|S_{\pm}|n>|^2}{T^2[(\gamma H_o + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}]} \tag{3.14}$$

The line width of the transition is given by the factor
$\rho(\omega)$. If the applied r.f. magnetic field is sufficiently weak so
that the last term in the denominator can be neglected, the
half-power point in the paramagnetic absorption is given by

$$(\gamma H_o + \omega) = \frac{1}{T_2}$$

When the applied r. f. magnetic field is large enough so the last term is not negligible, the half-power point is increased to

$$(\gamma H_o + \omega) = \sqrt{\frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2}}$$

The maximum absorption which occurs at resonance is also reduced because of the increase in the denominator. This condition is called saturation.

III. 2 The Reflection Cavity Maser

A maser can be constructed by placing a suitable paramagnetic material within a reflection cavity. The equivalent circuit of such a device is shown in Fig. 3.
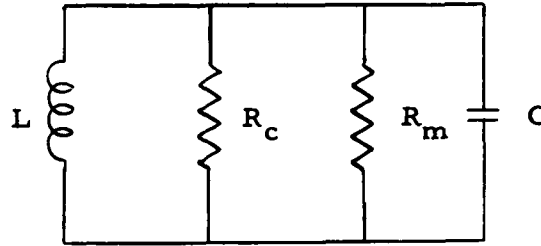

Figure 3

In this circuit, L and C represent the cavity. R_c represents the resistive and dielectric losses in the cavity walls and in the maser material. R_m is the absorption due to the imaginary part of the susceptibility, x''. The relation between x'' and R_m can be shown as follows. The power absorbed due to x'' is

$$P = -2\omega x'' H'^2 = -\frac{1}{2} \omega x'' H_x^2$$

The Q of a cavity due to losses arising from x'' alone is

$$Q = \frac{\omega X (\text{energy stored})}{\text{Power dissipated by } x''}$$

$$= \frac{2\omega \int H^2 dv}{-\omega x'' \int H_x^2 dv}$$

$$= -\frac{2}{x'' \eta} \tag{3.15}$$

where $\eta = \dfrac{\int H_x^2 dv}{\int H^2 dv}$

We recall that H' is one circularly polarized component of $H^{\perp}$; whereas, H is the total magnetic field intensity. Thus, η is always less than unity. If Q_0 is the Q due to R_c alone, the effective resistance representing x'' is

$$R_m = \frac{R_c Q}{Q_0} = \frac{R_c \cdot 2}{-x'' \eta Q_0} \tag{3.16}$$

The total conductance of the cavity at resonance is

$$\frac{1}{R_m} + \frac{1}{R_c}$$

The cavity is connected to a source and load through a waveguide. This coupling can be represented as a transformer as in Fig. 4. The source (load) can be transformed to the secondary side to give a new equivalent circuit as in Fig. 5.

In this maser the source and the load are the same. It can be shown that such a maser suffers from the fault that a large portion of the source power is dissipated in the source (load) impedance without being amplified by the maser.

This weakness is avoided by an insertion of a "circulator" between the maser cavity and the load and source. The circulator is a three-terminal-pair device in which energy flows only in one sequence: a→ b—→c. A maser using the circulator is shown in Fig. 6.

Now all the source power is incident on the maser. All the output (reflection) from the maser is delivered to the load.

The power delivered to the load is obtained by simply taking the reflected power from the cavity as computed from transmission line equations.
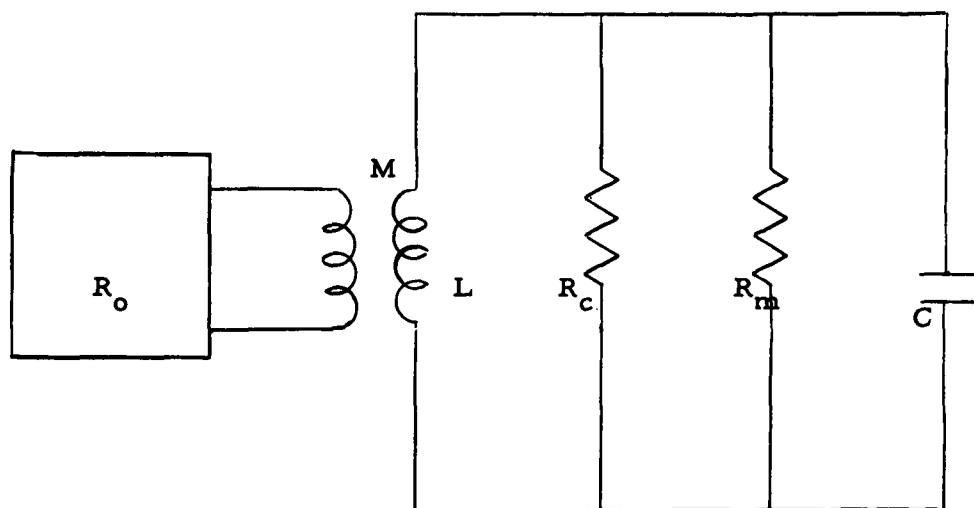
Figure 4
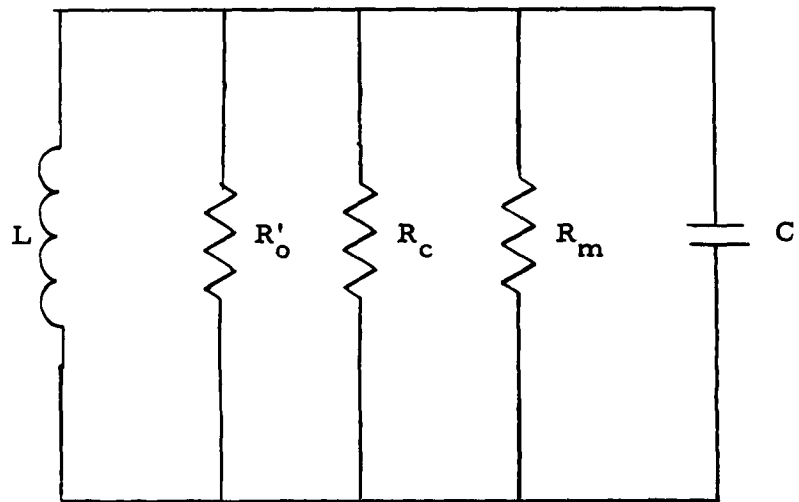
Figure 5
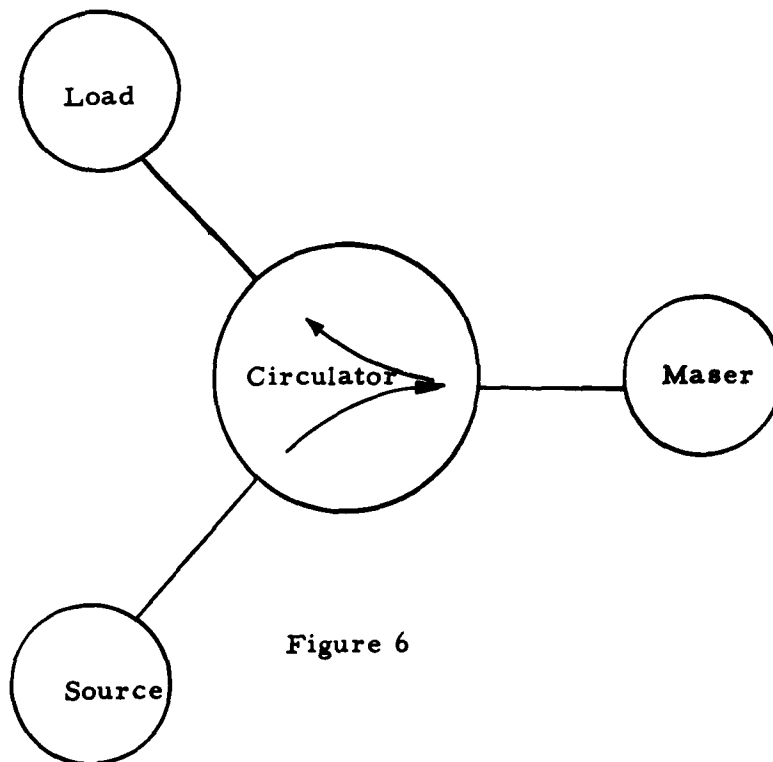
Figure 6

$$\Gamma = \frac{Z'_L - Z_o}{Z_L + Z_o} = \frac{Y_o - Y'_L}{Y_o + Y'_L} \qquad (3.17)$$

$$P_L = P_{in} \cdot \Gamma^2 \qquad (3.18)$$

For our maser we have

$$Y_o = \frac{1}{R'_o}$$

$$Y'_L = \frac{1}{R_m} + \frac{1}{R_m}$$

$$\Gamma = \frac{1/R'_o - 1/R_m - 1/R_c}{1/R'_o + 1/R_m + 1/R_c} \qquad (3.19)$$

The condition for amplification is that

$$\infty > \Gamma > 1$$

This is achieved when $\dfrac{1}{R_m} + \dfrac{1}{R_c}$ becomes negative so that the numerator of Eq. (3.18) is larger than the denominator. When $\dfrac{1}{R_m} + \dfrac{1}{R_c}$ is sufficiently negative to make the denominator vanish, the maser becomes an oscillator.

The gain of a maser was given as

$$\Gamma^2 = \frac{\left(\dfrac{1}{R'_o} - \dfrac{1}{R_m} - \dfrac{1}{R_c}\right)^2}{\left(\dfrac{1}{R'_o} + \dfrac{1}{R_m} + \dfrac{1}{R_c}\right)^2} = \frac{\left(\dfrac{1}{R'_o} - \dfrac{1}{R'_c}\right)^2}{\left(\dfrac{1}{R'_o} + \dfrac{1}{R'_c}\right)^2}$$

R'_c is the parallel resistance of R_c and R_m. To obtain gain, the following conditions are necessary or desirable:

(1) $R_m < 0$

(2) $|R_m| < R_c$

(3) $\dfrac{1}{R'_o} - \dfrac{1}{|R_m|} + \dfrac{1}{R_c}$ be as small a positive quantity as possible

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It is clear that to obtain amplification with a given R_c and R_o', we need a negative R_m with $|R_m|$ sufficiently small. This, in turn, demands that x" be sufficiently large. x", in turn, was given by (3.14) at resonance: $\frac{g^2\beta^2}{4\hbar}\Delta N\mu_{12}^2 T_2$. ΔN is the population difference between states 1 and 2, and μ_{12} is the matrix element of the spin moment between states 1 and 2. This shows that gain is easier to obtain when

(1) The quantity ΔN is large. In other words, we have a large inversion.

(2) μ_{12} is large.

(3) T_2 is long.

Going back to the expression for gain, we see that another way to obtain higher gain when the conditions for amplification are already satisfied, is to increase R_o'. For a given source and load impedance, this indicates that the coupling between the input-output waveguide and the maser cavity should be made small. While this is certainly true, it restricts the bandwidth.

The bandwidth of the maser can be limited by either the cavity bandwidth or the paramagnetic resonance line width of the material. The addition of the maser material with negative resistance serves to raise the Q. The expression for cavity bandwidth is

$$\Delta f = \frac{f}{Q} = f\left(\frac{1}{Q_L} + \frac{1}{Q_m} + \frac{1}{Q_c}\right) = \frac{f}{Q_c}\left(1 + \frac{R_c}{R_o'} + \frac{R_c}{R_m}\right) \quad (3.20)$$

For negative R_m

$$\Delta f = \frac{f}{Q_c}\left(1 + \frac{R_c}{R_o'} - \frac{R_c}{|R_m|}\right) \quad (3.21)$$

According to this expression, the cavity bandwidth of the maser cavity is a function of both R_o' and R_m.

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The bandwidth of the empty cavity, when it is decoupled from the load, is determined by Q_c. This is about 5,000-10,000. The corresponding bandwidth at 10 gc is about 2 mc. The actual cavity bandwidth for a maser can be considerably narrower or broader. The presence of R_o' broadens the bandwidth while the presence of a negative R_m reduces the bandwidth.

When the bandwidth of the maser is limited by the cavity, Terhune[40] shows that, although the gain-bandwidth product is not constant, the product $(G^{1/2}-1) \cdot B$ is constant for a given R_m and R_c.

$$(G^{1/2}-1) \cdot B =$$

$$\left\{ \left[\frac{1/Q_L - 1/Q_m - 1/Q_c}{1/Q_L - 1/Q_m + 1/Q_c} \right] - 1 \right\} \frac{f}{Q_c} \left(\frac{1}{Q_c} + \frac{1}{Q_L} + \frac{1}{Q_m} \right) = -2f \left(\frac{1}{Q_m} + \frac{1}{Q_c} \right)$$

For a negative R_m, it is $2f \left(\dfrac{1}{|Q_m|} - \dfrac{1}{Q_c} \right)$.

If the gain is increased by increasing R_o', the bandwidth is correspondingly decreased. The gain-bandwidth product is increased by decreasing $|R_m|$.

If we attempt to obtain a very broad bandwidth for a given R_m, R_o' must be made low. However, a limit to this approach is imposed by the bandwidth of the magnetic resonance. The solution for x'' was Eq. (3.18).

$$\frac{1}{T_2 \left[(\gamma H + \omega)^2 + \frac{1}{T_2^2} + \gamma^2 H'^2 \frac{T_1}{T_2} \right]}$$

In this expression resonance is given when $\gamma H_o + \omega$ is set to 0. That is,

$$\omega_r = -\gamma H$$

At a frequency $\omega' \neq \omega$,

$$\gamma H_o + \omega' = \Delta\omega, \text{ where } \Delta\omega = \omega' - \omega_r$$

$$x'' = \cfrac{1}{T_2[\,\Delta\omega^2 + \cfrac{1}{T_2^2} + \gamma^2 H'^2 \,\cfrac{T_1}{T_2}\,]}$$

$\gamma^2 H'^2 \dfrac{T_1}{T_2}$ is very small at power levels applicable to normal maser operation.[*]

The magnitude of x'' is $\frac{1}{2}$ of the maximum value when $\Delta = \dfrac{1}{T_2}$.
Although the line width of the resonance and the bandwidth of the
maser amplifier are not directly related, it is clear that $\dfrac{1}{T_2}$ gives a
reasonable measure of the bandwidth of the amplifier when it is
limited by the line width of the material. This is certainly the case
for non-resonant masers such as traveling-wave masers which
we have not discussed. For very wide-band amplifiers, T_2 must
be short.

Up to this point, the relaxation time T_1 has not been mentioned
explicitly in the maser properties. Yet, it is probably the most
important parameter for maser materials. T_1 enters the problem
through the factor $(N_2 - N_1)$ in the expression for x'', which was
already seen to be the determining factor in the gain of a maser.

Bloembergen's[4] three-level scheme, given in the intro-
duction, is to apply a sufficiently strong resonant excitation be-
tween the lowest and highest levels of three energy levels so that
their populations, N_1 and N_3, are almost equal. This excitation
is in competition with T_1, which represents a process that is
trying to maintain thermal equilibrium.

The excitation power required to make $N_3 = N_1$ can be
computed. At thermal equilibrium,

$$N_3 - N_1 = -\Delta N = \frac{N_o \Delta E}{2KT} \,.$$

---

[*] When this term is too large to be ignored, it will reduce x'',
and thereby, the gain. The maser is then in nonlinear operation.
It is then said to be saturated.

When $N_3 = N_1$, the deviation of ΔN from thermal equilibrium is just ΔN. The rate of energy loss through T_1 is then

$$P = \frac{\Delta N \cdot \Delta E}{T_1}$$
$$\cong \frac{N_o (\Delta E)^2}{2(KT)T_1}$$

It is instructive to estimate this quantity. Suppose $N_o = 10^{20}$

$$\Delta E = h \times 3 \times 10^{10} = 1.98 \times 10^{-16} \text{ ergs}$$

$$KT = 5.35 \times 10^{-16} \text{ ergs at } 4.2\,^{\circ}K$$

Then,
$$T_1 = 10^{-6}$$

$$P = 335 \text{ watts.}$$

This is the power which must be made up by the exciting field. It must be applied at a very low impedance (very strong magnetic field) for saturation. This can be seen from the saturation condition in the solution to Bloch's equation. In the actual maser, the cavity must be optimized for the signal frequency. We are not free to optimize the cavity for pumping. This factor and the additional losses in the cavity require that the pump provide several times as much power as that just estimated. It is evident that the requirement is prohibitive at $T_1 = 10^{-6}$. The effect of heat produced by such high power dissipation must also be considered.

To sum up, a short T_1 demands that the pump power be prohibitively high for maser operation. Such a high pump power raises the temperature of the maser even in a thermal bath. Because T_1 decreases rapidly with termperature, the pumping becomes inadequate and maser action cannot be obtained.

Finally, we consider the question of how the three required energy levels are to be obtained.

Confining ourselves to Zeeman energy levels, we require paramagnetic ions with an angular momentum of at least 1 to give the required three states (3=2J+1). In the discussion of the relaxation time T_1, it was shown that the presence of an orbital moment leads to a short relaxation time. Therefore, we require the orbital moment to be as close to zero as possible.

If the orbital moment were strictly zero, we are left with a pure spin state with (2 S+1) - fold degeneracy. If $S \geq 1$, the application of a magnetic field will yield the required number of levels as in Fig. 7. Unfortunately, this scheme will not work because the spin states are pure. The only transitions possible through a time-varying magnetic field are those which connect states whose values of M_s differ by 1. All of these transitions are resonant at the same frequency. It is not possible to pump between two states which are not adjacent to each other.

The situation is rescued by a small amount of orbital moment. It was shown that a small amount of orbital moment in the presence of a sufficiently anisotropic crystalline electrostatic field will partly remove the spin degeneracy without the application of a magnetic field. This was called zero-field splitting. When the magnetic field is added, the Zeeman energy is added to this initial splitting to completely remove the degeneracy. The total result is that

1) The resonant frequencies for different allowed transition are now different.

2) The spin states can become mixed so that many more transitions become allowed. Pumping is now possible between a number of levels.
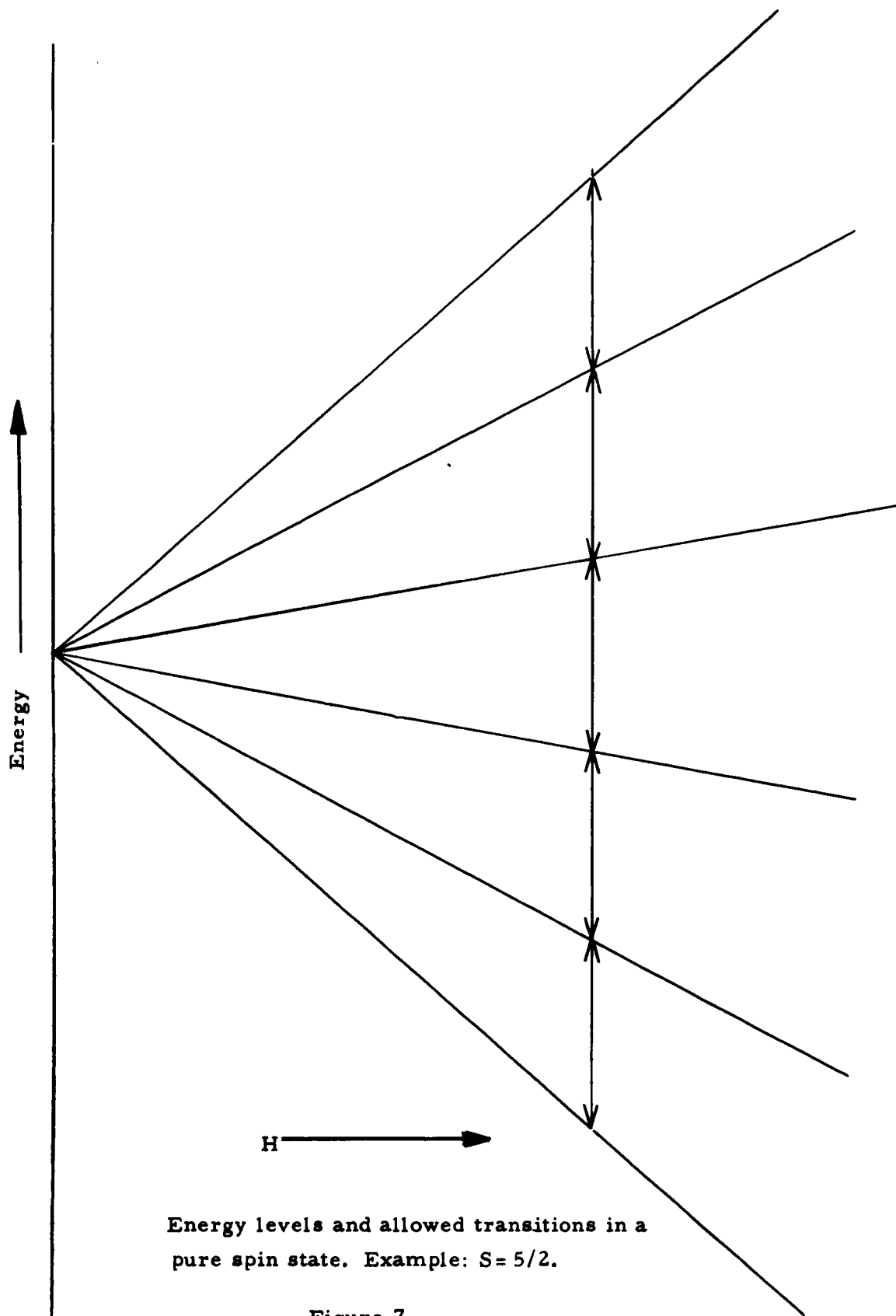
Energy levels and allowed transitions in a
pure spin state. Example: $S = 5/2$.

Figure 7

The Zeeman energy is proportional to the magnetic field. For a pure spin state the relation is

$$\Delta E = 2\beta H$$

for allowed transitions. For a signal frequency of 10 kmc, the field required is 3. 5 kilo-gauss. While this is not an unreasonable value, the magnetic field requirement becomes prohibitive for very much higher frequencies.

When zero-field splitting exists, the incremental ratio of frequency to magnetic field can be improved in some cases. But, the biggest advantage of the zero-field splitting is that it simply substitutes for Zeeman splitting. If S is the magnitude of zero-field splitting given in frequency, it reduces the required magnetic field by $\frac{S}{2.8 \times 10^6}$ from the value required for pure spin at the same frequency of resonance. In fact, if the proper zero-field splitting were avaliable, no magnetic field would be required. Masers based on this scheme have been discussed by Bogle and Symons.[41] It has been successfully operated by Kornienko[42] using Fe^{3+} impurity in Al_2O_3.

As the Zeeman energy becomes large compared to the zero-field splitting, the energy levels and states approach the condition for pure spin, and the difficulties associated with pure spin are encountered once again. For this reason, the upper frequency limit for a maser material is given approximately by the zero-field splitting. Thus, in order to extend the range of the maser to higher frequencies, materials with higher zero-field splittings must be developed.

III. 3 Summary

The conclusions of the preceding sections are summed here with some additional remarks.

The qualities desired of a good maser material are

(a) <u>A long relaxation time, T_1</u>

This is necessary if inversion is to be accomplished without excessive pump power and consequent heating of the maser material.

(b) <u>A large transition probability between the inverted states</u>

The susceptibility is proportional to the square of this quantity.

(c) <u>A large density of paramagnetic ions</u>

Inversion is proportional to the density, other things being equal. However, density should be kept low enough to keep magnetic ions separated. Excessively high density also leads to another type of relaxation which we have not mentioned: cross relaxation. This can lead to complications -- some good, some bad.[43]

(d) <u>A long T_2^*</u>

The susceptibility is proportional to T_2. There is an intrinsic part which is just inversely proportional to the density of paramagnetic ions. In many ions, there is an additional component due to the nuclear moments within the ion and in its neighbors. This should be reduced to a minimum. Should a large line width be required for a wide-band maser, the line can be broadened to the desired value by increasing the density of paramagnetic ions. This will also help (c).

(e) <u>Zero-field splitting equal to or larger than the intended maser frequency</u>

This is necessary to make pumping possible and to reduce the amount of magnetic field required. Because the

* See the following page.

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T_2, which is the characteristic time for destruction of the
magnetic moment normal to the dc magnetic field, is often
discussed in terms of two separate effects. One is a destruc-
tive interference of individual moments due to their having un-
equal precession frequencies. This can arise from slightly
different environments (position in a magnet gap, local distor-
tions in a crystal, etc.) for different spins. A slight varia-
tion in precession frequency among the spins causes spins,
which were initially all aligned, to lose their alignment in
a short time. This is called inhomogeneous T_2. The other
effect is the resonant interaction between spins of the same
precession frequency. The interaction removes the degeneracy
and thus broadens the line width. This type of line width is
described as "homogeneous T_2. "

The transient behavior of a spin system differs consider-
ably, depending on whether the line width is due to homo-
geneous or inhomogeneous T_2. However, in steady state,
as in a three-level maser, the distinction need not be made.

need for very high frequency masers is most urgent, high zero-field splittings are desired.

CHAPTER IV

A SURVEY OF POTENTIAL CRYSTALS FOR THREE-LEVEL MASERS

The qualitites desired in a crystal for three-level masers were discussed in a previous chapter. The problem of finding or making crystals with those desired qualities is now considered. This problem has been discussed previously by Singer. [44] There, only crystals which were available synthetically were considered. Here, consideration is extended to all crystals. The problem of finding or making crystals with those desired qualities can be divided into two parts. The first part is to choose the paramagnetic ion suited to the purpose. The second is to choose a suitable diamagnetic, dielectric solid to serve as a host for the paramagnetic ion. Of course, the two parts are not completely independent. The choice of one is bound to influence the other.

IV.1 The Paramagnetic Ion

The conditions which govern the choice are

1) Long T_1.

2) Long T_2.

3) At least three spin levels.

Van Vleck's theory, showed that spin-orbit coupling was the mechanism which was responsible for T_1. A long T_1 requires a small spin-orbit coupling constant λ and a small orbital moment. States which belong to terms of $L=0$ satisfy this requirement. In addition, even where $L \neq 0$, crystalline

fields of the proper symmetry were found to split the states in
the manifold of L in such a way that left a singlet state with the
lowest energy. In such a singlet state, the only orbital moments
present were those re-induced by spin-orbit coupling. This was
a second-order process proportional to $\dfrac{\lambda}{\Delta_j}$, where Δ_j is the
energy from the ground state to a higher orbital state j. There-
fore, in such cases, in addition to a small λ, large Δ_j's are
required for long T_1. This second condition dictates that the
ground orbital state be a singlet in an octahedral or cubic
symmetry. This is because the common environments of the iron
group are usually very close to one of these two symmetries.[+]
The exact, actual symmetry may be lower because of small
deviations, but the removal of degeneracy by such lower sym-
metries will not result in Δ's large engouh to produce good
quenching.

An exception is made for "non-magnetic" doublets dis-
cussed in Section II. 9. The component states in such a doublet
have quenched orbital moments. In addition, there is no first
order mixing between the components under spin-orbit coupling
so that the quenching is preserved.

The strong dependance of T_1 on λ must be noted in selecting
ions for long T_1.

With respect to T_1, the following combinations of ion and
symmetry are suitable.

Ion	Symmetry	Orbital Ground State
Ti^{3+}	cubic	non-magnetic doublet
V^{3+}	cubic	singlet
V^{2+}	octahedral	singlet
Cr^{3+}	octahedral	singlet
Cr^{2+}	octahedral	non-magnetic doublet
Mn^{2+}	any symmetry	L = 0
Fe^{3+}	any symmetry	L = 0
Fe^{2+}	cubic	non-magnetic doublet
Co^{2+}	cubic	singlet
Ni^{2+}	octahedral	singlet
Cu^{2+}	octahedral	non-magnetic doublet

[+] See the following page.

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Among the combinations listed, Fe^{3+} and Mn^{2+} are superior to the others. Cr^{3+} in an octahedral field is also better than the others because of the large energy gap between the singlet and the next lowest orbital and a small spin-orbit coupling. Trivalent ions have larger crystal field splitting and are, therefore, to be preferred. The non-magnetic doublets are generally inferior to the singlets. Cu^{2+} and Ni^{2+} have rather large values of λ. Therefore, they are less desirable.

The contribution by the ion to T_2 is the inhomogeneous broadening caused by the nuclear spin. When the hyperfine splitting is large, the lines outside the intended bandwidth of the maser do not participate in the maser action and is wasted. The effective density of the spins is reduced. The choice of ions with respect to T_2 falls on those ions with a minimum of nuclear spin. The desirable ions are $Fe^{2+, 3+}$ Ni^{2+} and $Cr^{2+, 3+}$, in the order given.

The condition $S > 1$ is also satisfied by $Fe^{2+, 3+}$, Ni^{2+} and $Cr^{2+, 3+}$.

Ions which satisfy all the conditions are Fe^{3+} in any symmetry, Cr^{2+}, Cr^{3+} and Ni^{2+} in octahedral symmetry and Fe^{2+} in cubic symmetry.

In addition to the iron group ions, the two S-state rare earths, Gd^{3+} and Eu^{2+}, display long T_1. The other rare earths have short relaxation times due to excessive orbital moment. Eu^{2+} is not suited for masers because of its nuclear moment.

The useful ions listed in the probable order of desirability are Fe^{3+}, Cr^{3+}, Gd^{3+}, Ni^{2+}, Cr^{2+} and Fe^{2+}.

$^+$By cubic symmetry, 8 negatively charged neighbors in a cube are designated. By octahedral symmetry, 6 negatively charged neighbors in an octahedron are designated.

IV. 2 The Host Crystal

The desired qualities in a host crystal are

a) Absence of paramagnetism for ferromagnetism on the part of the pure host crystal itself.

b) A minimum abundance and strength of nuclear moment, particularly in the ions immediately adjacent to the paramagnetic impurity.

c) Sufficient asymmetry to produce a large zero-field splitting.

d) Good stability. Particularly, resistance to thermal stress and moisture.

e) A small unit cell, so that all the paramagnetic ions are magnetically equivalent.

f) If possible, cations of the same valence as the intended paramagnetic substitute.

g) Cations whose ionic radii are similar to the radii of the intended paramagnetic substitute.

h) If possible, sufficiently low symmetry to remove orbital degeneracies in the ground state.

i) Very high resistivity.

The condition on nuclear moment rules out a very large number of the most commonly available crystals. All the halides are ruled out because of their nuclear spin. Also ruled out are all the hydrated crystals because of the nuclear spin of hydrogen. For the same reason, most organic crystals are not suitable.

The crystals which may be suited are the oxides, carbonates, sulphates, tungstates, chromates, silicates, silicides, sulphides and carbides of metals which are not in themselves paramagnetic and which have a low abundance of nuclear moment.

The condition that large zero-field splitting should result is not as easy to apply. The theoretical relation between the zero-field splitting and the strength and symmetry of the crystalline field is well known, but so far, the numerical values of

the parameters which enter into the expression are not known with sufficient accuracy to allow even approximate calculation. We do not know, however, that a cubic symmetry cannot cause a zero-field splitting in $S=1$ or $S=3/2$. Therefore, in the case of the paramagnetic ions Cr^{3+} or Ni^{2+}, a cubic symmetry must be avoided. A word of caution is in order here. The symmetry, which in involved, is the point symmetry of the paramagnetic ion site and not of the crystal as a whole. These two symmetries usually differ, the point group being lower.

It was noted previously that the positions of the negatively charged neighbors about the metallic cation are usually very close to octahedral when the radius of the metallic ion is small compared to the radius of the negative neighbors. When the negative neighbor is oxygen, this condition is usually satisfied. We can speculate that this relation is not followed as closely in the case where the neighboring oxygens belong to tightly-bound complexes such as SiO_4, SO_4, CO_3, CrO_4 or WO_4. In such cases, the oxygens may not be free to pack themselves as closely and regularly about the metallic ion. The regularity can also break down when the metallic ion is comparable to or larger than oxygen in radius.[45]

The unit cell should be small in order that the paramagnetic ions are not placed in a number of sites which do not give the same spectrum. Such a case reduces the effective number of ions participating in any one resonance except for special orientations of the magnetic field. By a large unit cell we mean that the unit cell contains a large number of molecules. Magnetically, many of these may be equivalent. Two sites related by inversion, for example, are always equivalent magnetically because of the inversion symmetry of all paramagnetic spectra. The number of nonequivalent sites is also reduced when the spin value S is small or the symmetry is

very high, for we have seen that, in these cases, details of the symmetry fail to be registered in the magnetic spectra. If the sites in a unit cell are nonequivalent only because of these details which cannot be registered in the paramagnetic spectrum, the sites become equivalent magnetically. In many cases, even when the sites are not completely equivalent, there are ample special orientations which make them equivalent to make them useful in maser work.

The requirement of proper valence is not a stringent one. It is true that extensive replacement of the cation by single impurity requires the valence state of the replacement ion to be the same as the original ion. For dilute substitutions of less than .1%, this is not necessary, particularly if the crystal is not annealed. The excess or deficiency of charge can be neutralized by a compensating impurity or by an additional anion in the nearest interstitial. If the interstitial anion or charge compensating second impurity is close enough to the paramagnetic ion, the symmetry about the ion is altered suf- ficiently to influence the spin resonance spectrum. Tinkham[28] has observed such spectra for Cr^{3+} in ZnF_2. Very often, however, the compensation is sufficiently far away so that no detectable change occurs in the symmetry about the paramagnetic ion.

Until recently, it was believed that substitutions could not occur if the ionic radii of the ions to be exchanged differed by more than 15%. However, the research in maser materials within the last two years has shown that substitutions up to the order of .1% may be possible in many cases.[46]

The requirement that the resistivity be very high is obvious. Even a small resistivity would greatly reduce the Q of the maser cavity. Furthermore, at microwave fre- quencies, conductivity leads to skin effect which removes the

interior of the crystal from participation in maser action. In
this respect, the sulphides must be examined carefully. Some
of the sulphides are fairly good conductors or semiconductors.
Galena (PbS) is a good example.

Some of the sulphides have been used as hosts for para-
magnetic impurities. Mn^{2+} in ZnS and Eu^{2+} in SrS are notable
examples. Sulphides are not always ionic, and many of them
may prove unsuitable for masers. The same situation exists
with carbides and silicides.

Armed with the considerations stated above, we can
examine the compilation of inorganic compounds given in the
Handbook of Chemistry and Physics,[47] Wyckoff's Crystal
Structures[48] and the International Tables for X-Ray Crystallo-
graphy.[49] Two facts stand out in such an examination.

a) The lack of suitable crystals which give a cubic
(8-fold coordination) symmetry. The CaF_2 (fluorite) structure
is the only such structure. All but one member of this class
must be rejected for one reason or another. CeO_2 is the only
possibility. Unfortunately, it is accurately cubic. In addition,
its quadri-valent cation makes it less useful. Three other
structures have 8-fold coordination, but they are very far from
cubic. They are the $ZrSiO_4$ (zirzon) structure, $CaWO_4$
(scheelite) structure and ZrO_2. Of these, $ZrSiO_4$ and $CaWO_4$
are very interesting for other reasons. ZrO_2 is difficult to
use because of the quadri-valent cation and its four nonequi-
valent sites.

b) The remarkably small number of suitable crystals
with trivalent cations. La_2O_3 is practically the only promising
one besides the already well-known Al_2O_3 (corundum).

A list of some crystals which may be suitable is given
below. This is by no means complete. On the other hand, many
of these crystals may be unsuitable because of some factor
which escaped the author's consideration.

$BaCO_3$, $BaCrO_4$, BaO, $BaSO_4$, $BaWO_4$, $BaSiO_3$

$CdCO_3$, $CdSiO_3$, $CdSO_4$, $CdWO_4$

$CaCO_3$, $CaSiO_3$, $CaCrO_4$

CeO_2

La_2O_3

$PbCO_3$, $PbCrO_4$, $PbSO_4$, PbO, $PbSO_4$, $PbSiO_3$

$PbWO_4$, MgO, $MgCO_3$, $MgWO_4$, $MgSiO_3$, SiO_2

$SrCO_3$, $SrCrO_4$, SrO, $SrSiO_3$, $SrSO_4$, $SrWO_4$

SnO, SnO_2, $SnSO_4$

TiO_2

$ZnCrO_4$, $ZnCO_3$, ZnO, $ZnSiO_3$, $ZnSO_4$

ZrO_2, $ZrSiO_4$

The exact structures of many of the silicates are not yet known. The metasilicates of known structure have very large unit cells. $CaSiO_3$, for example, has 12 molecules in a unit cell. Perhaps, the only interesting crystal in the group is zircon, which has four molecules in a unit cell. Fortunately, all the sites are equivalent. The local symmetry is 42m. 8 oxygens form the nearest neighbors.

The sulphates which are listed are all of the same orthorhombic structure. There are four molecules in a unit cell. However, they are made up of pairs, related by inversion so that only two sites are nonequivalent magnetically. The radii of the cation are very large. This results in a high coordination number (12) and low point symmetry (m). All the cations are divalent.

The carbonates are of two distinct structures. The smaller cations result in the trigonal structure of $CaCO_3$ (calcite). The point symmetry at the cation site is also trigonal (C_{3i}). The two sites in the unit cell are not equivalent. The structure of the carbonates with large cations is similar to the sulphates. The point symmetry about the cation is m. The cations are surrounded by

six oxygens in a distorted octahedron.

The tungstates have already been successfully exploited as hosts for paramagnetic ions. They are of two types. Those with large cations form tetragonal crystals. There are four molecules in a unit cell, but all are equivalent. This is a particular virtue of this structure. Tungstates with small cations form monoclinic crystals which are isomorphous (have the same structure and size; therefore, interchangeable) with most of the tungstates of the iron group. They have two molecules in a unit cell. The two cation sites are equivalent. Both types have shown great promise in maser applications.

The chromates are divided into three structures. Those with big cations ($CaCrO_4$) have the same structure as $ZrSiO_4$ and are very suitable. The four cation sites in a unit cell are all equivalent. The local symmetry is 42m. Another structure is that of $ZnCrO_4$ and $CdCrO_4$. These crystals are orthorhombic. The local symmetry is $\frac{2}{m}$. The four cations in a unit cell are all equivalent. The coordination around the cation is a distorted octahedron. $PbCrO_4$ is monoclinic and has two nonequivalent sites.

The oxides are also divided into a small number of groups. The oxides MgO, CaO, BaO, SrO and CdO are accurately cubic with exact octahedral coordination about the cation.

A very interesting crystal is La_2O_3. It has only one molecule in a unit cell. The two La^{3+} in the unit cell occupy sites which are related by inversion, making the sites equivalent magnetically. The local symmetry is 3m. Furthermore, it is an ideal host for trivalent ions. Gd^{3+} in La_2O_3 should be an ideal combination.

TiO_2 and SnO_2 constitute another class. The unit cell contains two cation sites which are not equivalent. The local symmetry is orthorhombic. The apparent success of TiO_2 as a maser material raises hopes that other crystals with

quadri-valent cations may be successful. CeO_2 with the accurately cubic fluorite structure may be such a crystal.

PbO and SnO have a tetragonal crystal with 2 cations per unit cell. The local symmetry is given as 4mm. The two sites are equivalent magnetically. This crystal is not strictly ionic, and its suitability is a question mark.

CONCLUSION

The following combinations of crystal and paramagnetic impurity seem to be particularly promising.

La_2O_3 It should be an ideal host for Gd^{3+}. It should also be very good for Fe^{3+}. However, the large difference in ionic radii causes some concern. The 7-fold coordination does not permit us to say what the orbital ground state of Cr^{3+}, Ni^{2+}, Cr^{2+} and Fe^{2+} will be with any assurance. They may be favorable. Rare earths are difficult to separate from each other. Growing pure La_2O_3 without other rare-earth impurities may be difficult. The line broadening due to the nuclear moment of La should not be too large because La would not be the nearest neighbor of paramagnetic impurities.

$CaCrO_4$ Fe^{3+} and Gd^{3+} should be good. Again, the large difference in ionic radii of Ca^{2+} and the iron group impurities causes some concern. The 8-fold coordination is far from cubic so that it is difficult to say what the orbital ground states for Cr^{3+}, Ni^{2+}, Fe^{2+} and Cr^{2+} will be. They may be favorable. Irregular coordination may result in large zero-field splitting.

$ZnCrO_4$ ⎫
$CdCrO_4$ ⎬ In spite of having four molecules in a unit cell, all sites are equivalent. The point of symmetry is only mm. The 4-fold coordination about the Zn, Cd, sites make them particularly attractive. In some structures the positions of Cr^{6+} and the other metallic cation become interchanged.

$ZrSiO_4$ The situation is identical with $CaCrO_4$.

$CaWO_4$ ⎫
$BaWO_4$ ⎬ These crystals have already been examined with Fe^{3+}.
$SrWO_4$ ⎭ and Gd^{3+}.[13] The results have been excellent. The success in introducing Fe^{3+} gives hope that other crystals with large cations will likewise accept Fe^{3+}. The coordination is 8-fold but far from cubic. The absence of any report on Cr^{3+} may indicate that the sign of the crystalline field puts the orbital triplet lowest.

$MgWO_4$ ⎫
$ZnWO_4$ ⎬ These crystals have shown very good characteristics with Fe^{3+} impurity.[12]
$CdWO_4$ ⎭

The following crystals will yield two spectra for ions with $S \geq 2$. Nevertheless, they show features which warrant investigation.

$CaCO_3$ ⎫
$MgCO_3$ ⎬ These crystals should be good hosts for Fe^{3+}, Gd^{3+}, Ni^{2+} and Cr^{2+}. The coordination is close to octahedral
$ZnCO_3$ ⎭ assuring a singlet orbital state for Ni^{2+} and Cr^{2+}. Structure is fairly similar to Al_2O_3. The nuclear spin content is exceptionally low.

$BaCO_3$ ⎫
$SrCO_3$ ⎬ These crystals also feature low nuclear moment and an octahedral coordination.
$PbCO_3$ ⎭

$PbCrO_4$

$\left.\begin{array}{l}BaSO_4 \\ SrSO_4 \\ PbSO_4\end{array}\right\}$ The very high (12) and irregular coordination makes it difficult to make any predictions. If Fe^{3+} or Gd^{3+} can be introduced, large zero-field splitting may result. It is difficult to predict the degeneracy or near degeneracy of the orbital ground state for Cr^{3+}, Cr^{2+}, Fe^{2+} or Ni^{2+}.

$\left.\begin{array}{l}TiO_2 \\ SnO_2\end{array}\right\}$ TiO_2 crystals with Fe^{3+} have already shown huge zero-field splitting.

Other interesting combinations are as follows:

$\left.\begin{array}{l}MgO \\ BaO \\ CaO \\ CeO_2\end{array}\right\}$ The pure octahedral field can give zero-field splitting in Fe^{3+} and Gd^{3+}. Nevertheless, the high symmetry makes them difficult to use in three-level masers. This is the only crystal with 8-fold coordination cubic symmetry about the cation. Fe^{2+} should be very interesting if it can be made to substitute the quadri-valent Ce. Very large zero-field splitting should result.[18]

Before concluding this section, two more classes of crystals deserve mention.[49] They are the borates and the phosphates. These crystals were excluded from the preceding discussion because of their abundant nuclear spin. However, as in Al_2O_3, the nuclear spins reside not in the immediate neighbors but in the next nearest neighbors of a paramagnetic impurity. Therefore, the contribution to the line width is small. The borates are particularly attractive because they form stable crystals, and they generally form crystals with trivalent cations. There is a lack of literature on the borates. However, it is found that $LaBO_3$ has the same structure as calcite. It should be an ideal host for Fe^{3+}, Gd^{3+} and Cr^{3+}. The approximately octahedral arrangement of oxygens around the cation should give a singlet orbital state as the ground state for Cr^{3+}.

IV. 3 Availability of Crystals

Most of the crystals in the preceding section have been known as natural crystals: some as gems and semiprecious stones. Various impurities are present in natural crystals, and paramagnetic resonance due to such impurities have been studied. Only in a few fortunate instances, however, do the crystal and impurity form the combination desired in a three-level maser. Even when the right combination is present, the concentration may not be optimum; an abundance of other undesirable impurities may be present; or single crystals may be too small. A crystal must be available synthetically before it can be a practical maser material. Only then can all the properties be controlled to specifications. The particular prominence of ruby $(Al_2O_3:Cr)$ as a three-level maser material is largely due to its availability in synthetic form. TiO_2 is also investigated because it is available synthetically.

Growing synthetic crystals is not necessarily difficult. In a great many cases, it is simply the lack of sufficient scientific or commercial incentive which has resulted in their neglect. Perhaps, in a number of crystals, all that is required is to try. However, the very great difficulty experienced in the growth of synthetic diamond and quartz should restrain one from too much optimism. Generally speaking, crystals which can be melted at reasonable temperature and pressure, or crystals which can be dissolved in some solvent are probably easiest to synthesize. For example, hydrated crystals can be grown readily from solution. The very insoluble $BaSO_4$ is difficult to grow. $CaWO_4$ can be grown from a melt. Crystals such as $CaCO_3$

decompose upon heating so that growth from a melt is not possible.

Among the crystals which were classified as promising or interesting in the preceding section, the following have been grown: MgO, $CaWO_4$, $MgWO_4$, $ZnWO_4$, $CdWO_4$, and TiO_2.

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